



RAI 337

**Water Recovery Study**

**Contract NASw-520 with  
The National Aeronautics and Space Administration  
Ames Research Center, Moffet Field, California**

**Report for Period  
September 7, 1962 - March 7, 1964**

*R*

**Richard Everett Jr.  
Eric Meier  
George Odian  
Ernest Henley  
Arnold Katz  
Martin Hofstetter**

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## FOREWORD

The work described in this report, "Water Recovery Study," was performed under Contract NASw-520 with the National Aeronautics and Space Administration.

The authors wish to acknowledge the assistance of Messrs. Elliot Ratchik and Orest Pobihushka during the early stages of the program. The authors also take this opportunity to express their appreciation to Professor S. Loeb, Dr. S. B. Tuwiner, Dr. D. R. Young, Mr. P. Quattrone, and Mr. A. Inglefinger for many fruitful discussions throughout the course of the program.

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The research program initiated by NASA at RAI in September 1962 has resulted in the demonstration of a system of water recovery from urine based upon ultrafiltration preceded by electrolytic urea removal (the EUF system). The components of the experimental system have been developed and tested. From this it is expected that the final system will weigh less than 30 pounds and have a theoretical power consumption of 24 watts/9.9 lb urine.

The two essential steps in the process are:

1. Electrolysis - The chloride ion in the salt is converted to  $\text{Cl}_2$ , which in turn forms hypochlorous acid,  $\text{HOCl}$ . The  $\text{HOCl}$  oxidizes the urea and other organic matter to  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Concurrently, the evolved hypochlorite serves to sterilize the urine, as independent E. Coli counts have demonstrated.

2. Ultrafiltration - The electrolyzed urine is pumped through a cellulose acetate membrane which rejects  $\text{NaCl}$ , but passes water. Water meeting USPHS specifications has been recovered from the subject process.

A continuing research program directed toward elucidating the fundamental mechanisms of the electrolysis and ultrafiltration process was conducted. The salient parameters studied were:

a. Electrolysis - Rate of denitrification of synthetic versus real urine.

b. Ultrafiltration - Study of pertinent physical parameters in the ultrafiltration of model and real denitrified urines.

*Auth*

## 2.0 INTRODUCTION

### 2.1 The Need for Water Recovery

Recent advances in aerospace technology allow for more ambitious manned flight programs involving larger crews and longer duration missions. These projections are, of necessity, accompanied by many new problems, not the least of which is that of life support.

One extremely important facet of the life support problem is that of providing sufficient ingestion water for long-range missions. In order to illustrate the magnitude of the water supply problem, one may make a simple calculation. The maintenance of a normal metabolic water balance requires a daily water ingestion of 2200 grams (4.8 pounds) per man.<sup>1</sup> Using this figure one may calculate the weight of water required as a function of crew size and mission duration as indicated in Table 1 below:

Table 1

Water Requirement in Pounds as a Function of Crew Size and Mission Duration

Crew Size in Number of Men	Mission Duration in Days				
	1	15	30	90	365
1	4.8	72	144	432	1752
3	14.4	216	432	1296	5256
5	24.0	360	720	2160	8760

Thus, a three man crew on a ninety day mission has a water ingestion requirement of 1296 pounds. The storage of this amount of water within the confines of the space capsule imposes extreme penalties on the requisite capsule volume and rocket thrust. With these considerations in mind, the desirability of water recovery from urine and other waste sources is readily apparent.

## 2.2 Program Objectives

The prime objective of the program was the determination of feasibility of potable water recovery from human urine via membrane ultrafiltration.

Within this framework, the subject program was subdivided into the three areas of study delineated below:

- a. Synthesis of superior membrane filters.
- b. Development of requisite pre- and post-treatments.
- c. Evaluation of ultrafiltration parameters.

Based on the experimental results gathered, it was an additional objective of the program to develop a preliminary design of a unit possessing the following characteristics:

- a. aerospace applicability from the standpoints of weight, power, and volume requirements,
- b. operational simplicity,
- c. ease of maintenance.

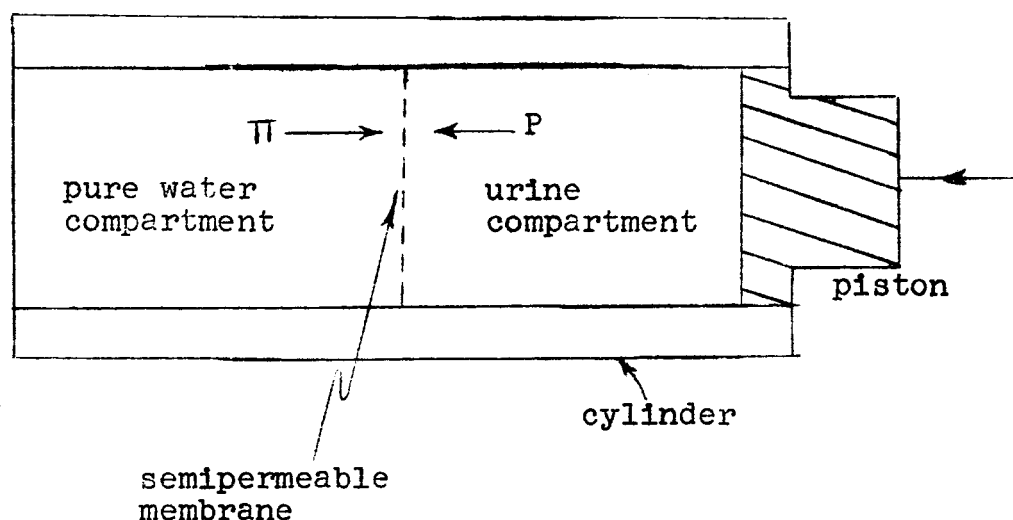
### 3.0 TECHNICAL BACKGROUND

#### 3.1 Ultrafiltration - General

Ultrafiltration, or "reverse osmosis" as it is sometimes referred to, is an extreme type of filtration differing markedly from the common laboratory solid-liquid resolution technique. In an ultrafiltration process one attempts the resolution of a solute-solvent pair (solution) through the use of a membrane filter which can successfully discriminate against the former. Inasmuch as the solutes are frequently at the Angstrom level in size, the pores of the membrane filter are of necessity extremely small. Thus, the translation into a successful solvent (water) recovery process requires relatively large driving (pressure) forces. In order to illustrate let us consider the cell depicted in Figure I:

Figure I

Model Ultrafiltration Cell



The model cell depicted consists of two compartments, water and urine containing, separated by a semipermeable membrane. The term "semipermeable" refers to the ability of the membrane to transmit water in either direction without allowing the

solute species in the urine to enter the water compartment. In the absence of any external driving force imposed by the piston, water will flow spontaneously from the left (water) to the right (urine) compartment under the influence of the osmotic pressure,  $\pi$ . This process is the familiar "osmosis" and is of course undesirable. If the piston is moved toward the left, one can exert a pressure,  $P$ , over and above the osmotic pressure,  $\pi$ , thus reversing the normal direction of water flow. Thus, the problem in the subject program lies in the fabrication of membrane filters capable of holding back the solute species while concurrently allowing for the high level transmission of potable water.

In view of the ultimate life support requirement to be imposed on the ultrafiltration system, information on recovery rates as a function operating pressure,  $P$ , and feed osmotic pressure,  $\pi$ , is required. The work of Merten<sup>2</sup> and co-workers on the demineralization of sea water via membrane ultrafiltration is particularly significant in this area and merits mention at this time. In these studies the flux was determined as a function of operating pressure and feed osmotic pressure for salt water solutions of known concentration. The following expression was derived from the experimental data:

$$3.1A \quad \phi = K(P - \pi)$$

where  $\phi$  = water transmission rate (flux)

$K$  = membrane transmission coefficient

$P$  = operating pressure

$\pi$  = osmotic pressure of the feed solution

This expression above may also be written in the form:

3.1B

$$\phi = KP - K\overline{\Pi}$$

where  $KP$  = gross "driving" flux

$K\overline{\Pi}$  = gross "retarding" flux

$KP - K\overline{\Pi}$  = net flux

Thus, for a given membrane transmission coefficient,  $K$ , the relative fluxes through membrane filters are (1) increased by increasing operating pressure and (2) decreased by increasing osmotic pressure of the feed solution.

3.2

### Urine - Raw Material for Water Recovery

Urine, by virtue of its position as a metabolic waste product is subject to wide variation in both qualitative and quantitative characteristics. These variations are primarily caused by dietary considerations. In order to establish a frame of reference one can consider the composition in Table 2 reported<sup>3</sup> as the typical excretion for a healthy male during a 24-hour interval.

Table 2  
Composition of Typical<sup>3</sup> Human Urine

Constituent	Average Daily Excretion in Grams
Water	1200.0
Solids	60.0
Urea	30.0
Uric Acid	0.7
Hippuric Acid	0.7
Creatinine	1.2
Indican	0.01
Oxalic Acid	0.02
Allantoin	0.04
Amino Acid Nitrogen	0.2
Purine Bases	0.01
Phenols	0.2
Chloride as Sodium Chloride	12.0
Sodium	4.0
Potassium	2.0
Calcium	0.2
Magnesium	0.15
Sulfur, total, as S	1.0
Inorganic Sulfates as S	0.8
Neutral Sulfur as S	0.12
Conjugated Sulfates as S	0.08
Phosphate as P	1.1
Ammonia	0.7

Thus, normal human urine contains 1200/1260 x 100 or approximately 95% by weight of available water and as such is an extremely important raw material for potable water recovery.

### 3.2.1 Osmotic Pressure of Human Urine

Reference to equation 3.1B indicates the "retarding" flux to be of the form  $K\pi$ , viz., osmotic pressure dependent. For this reason it is important to determine the magnitude of the osmotic pressure of untreated as well as treated urines in order to predict the effects on flux,  $\phi$ , as well as recovery yields.

Osmotic pressure,  $\pi$ , is a colligative property dependent on number rather than kind of species present in a given solution. Thus, if one knows the constitution of a given

solution it is possible to determine the individual solute species contributions toward overall osmotic pressure. Assuming a 38.1 psi contribution per M/10 molality as measured for sucrose solutions<sup>4</sup>, one may calculate the contributions of the individual species by multiplying their respective molalities by 38.1 psi/M/10 molal. The calculations are tabulated below in Table 3.

Table 3

Calculated Osmotic Pressure Contribution of Prime Urine  
Contaminant Species

Contaminant	Molal Concentration	Contribution toward Osmotic Pressure, $\frac{\text{lbs.}}{\text{in.}^2}$
Urea	0.41	156
Chloride Ion	0.28	107
Sodium Ion	0.14	53
Potassium Ion	0.04	16
		Total = 332 psi

This figure, 332 psi, is in good agreement with that of Schoen<sup>5</sup> and co-workers who consider a value of 300 psi for the osmotic pressure typical of urine.

Freezing point depression,  $\Delta T$ , like osmotic pressure,  $\Pi$ , is a colligative property, that is concentration rather than solute character dependent. In view of the relative ease of measuring freezing point depressions it was decided to use this method as a means of osmotic pressure evaluation. The freezing point depression,  $\Delta T$ , exhibited by a solution relative to its pure solvent may be expressed by the following equation:

3.2.1A

$$\Delta T = K_1 m$$

where  $\Delta T$  = freezing point depression exhibited in degrees centigrade.

$K_1$  = a cryoscopic constant, the freezing depression exhibited by a 1 molar solution of an unionized solute, in degrees centigrade per mole.

$m$  = number of solute moles present per unit volume, i.e., molarity on a moles per liter basis.

It must be noted that a 1 molar sodium chloride solution gives rise to a two-fold depression in view of its ionization to two independently depressing species.

Osmotic pressure,  $\pi$ , like freezing point depression is a colligative property and thus concentration dependent and may be expressed by the following equation:

3.2.1B

$$\pi / m = K_2$$

where  $\pi$  = osmotic pressure in pounds per square inch.

$m$  = number of solute moles per unit volume, viz. molarity on a moles per liter basis.

$K_2$  = proportionality constant.

Equating of equations 3.2.1A and 3.2.1B yields the following expression:

3.2.1C

$$\pi = \frac{K_2}{K_1} \cdot \Delta T$$

The constants  $K_2$  and  $K_1$  may be independently determined from osmometric and freezing point depression measurements on solutions of known concentration respectively. Thus, equation 3.2.1C may be written in form

$$\pi = K_3 \cdot \Delta T$$

where  $\pi$  = osmotic pressure of a given solution in lbs./in.<sup>2</sup>

$K_3 = K_2/K_1$  = pressure-temperature proportionality factor in lbs./in.<sup>2</sup>-degrees.

$\Delta T$  = Freezing point depression in degrees.

### 3.2.2 Chemistry of Human Urine Contaminants

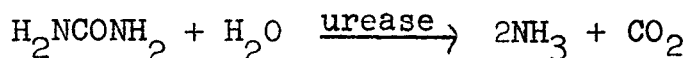
In view of the ultimate potability requirement and the possible chemical treatments one may employ, a discussion of the chemistry of urine is in order.

Referral to Table 2 indicates that urea is by far the most concentrated single contaminant species present in human urine and as such its chemistry is of interest. The prime physical and chemical properties of urea are summarized in Table 4.

Table 4

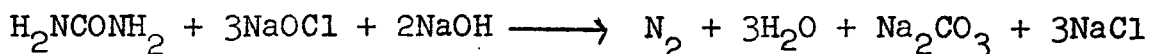
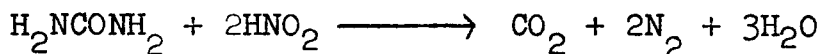
#### Summary of Physical and Chemical Properties of Urea

1. Structural formula  $\text{H}_2\text{N}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$
2. Molecular Weight<sup>6</sup> - 60.06
3. Solubility in Water<sup>6</sup> - 119.3 grams/100 gram  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ .
4. Principle Reactions
  - a. Hydrolysis

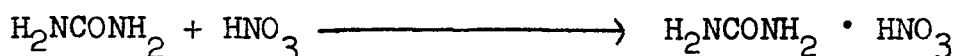
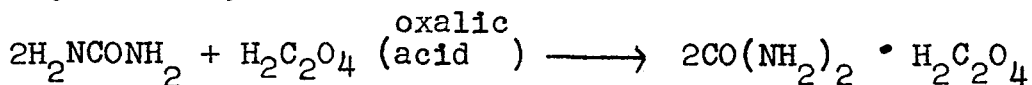


The above reaction is catalyzed by bacterial species in general and very rapidly under the influence of the enzyme, urease.<sup>7</sup>

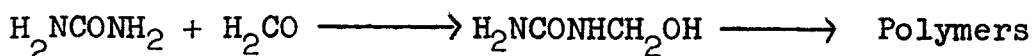
#### b. Oxidation<sup>8</sup>



#### c. Acid-Base<sup>8</sup>



#### d. Condensation<sup>9</sup>



### 3.3 Ultrafiltration Membrane Filters

The study of ultrafiltration and ultrafiltration membrane filters has classically been associated with the problems of osmosis and the semipermeable membrane. The first mention of the process now known as ultrafiltration is attributed to Schmidt<sup>10</sup> who studied aqueous solutions of protein and gum arabic. Bechhold<sup>11,12,13</sup> studied filter papers impregnated with acetic acid-collodion and was able to prepare membrane filters of various porosities by adjustment of the collodion:acetic acid.

Membrane filters suitable for application in the area of aqueous solution ultrafiltration have one common characteristic, that is, the ability to effectively sorb water. Thus, the common characteristic is the possession of hydrophilic sites. Among the host of materials which possess the aforementioned characteristics collodion, cellophane, and cellulose acetate have received fairly intensive investigation as membrane filters. In order to simplify discussion the classes of solutes which must be rejected in an effective ultrafiltration may be subdivided into non-electrolytes and electrolytes.

#### 3.3.1 Ultrafiltration of Non-Electrolytes

The most extensive study in the ultrafiltration of non-electrolytes is attributed to McBain<sup>14</sup> who studied ultrafiltration of various aqueous solutes through cellophane membranes. The results of these studies are shown in Table 5.

Table 5

Effect of Molecular Weight on Batch Ultrafiltration<sup>14</sup>

Material	Molecular Weight	Percent Rejection
Glycerol	92	2.2
Dextrose	180	7.0
Sucrose	342	14.9
Raffinose	504	18.1

It was found that the percent rejection was only slightly affected by concentration in the case of sucrose whereas electrolytes showed a strong concentration dependence. Ambard and Trautman<sup>15</sup> likewise studied the ultrafiltration of non-electrolytes and found the percent rejection proportional to number of constituent atoms. The results of their studies are shown in Table 6.

Table 6

Ultrafiltration of Non-Electrolytes

Substance	Number of Constituent Atoms	Percent Rejection
Urea	8	0.5
Glucose	24	5.0
Sucrose	45	9.0

These workers also found that percent rejection was virtually independent of concentration in experiments employing a ten-fold spread of urea concentrations.

The most popular current theory as regards the mechanism of rejection of non-electrolytes entails a sieving process. Neglecting adsorption and blocking phenomenon Manegold and Hoffman assumed the sieving to be expressible by the equation 3.3.1A

### 3.3.1A

$$S_K = \frac{C_f}{C_s}$$

where  $S_K$  = sieve constant (independent of concentration)

$C_f$  = instantaneous filtrate concentration

$C_s$  = instantaneous filtrand concentration

On the basis of numerous simplifying assumptions it is possible to calculate  $S_K$  as a ratio of pore size to particle size. The assumptions include

- (1) The membrane filter is ideally isoporous
- (2) Adsorption and blocking do not occur
- (3) Every solute species is travelling vertically downward when its center passes the plane of the surface and in order to penetrate a pore it must reside wholly within the walls of the pore, i.e., its center must be within a circle of radius  $r-R$  where  $r$  is the pore radius and  $R$  the solute radius.
- (4) At the pore entrance there is no radial velocity component whereas the vertical velocity has a parabolic distribution.
- (5) The filtrand is homogeneous.

With these conditions satisfied, the sieve constant can be expressed as a function of pore and solute radii alone.

Qualitatively, then, for a given membrane where  $r$  = constant, the increasing radius of the solute  $R$  makes alignment within the  $r-R$  radius increasingly difficult resulting in improved rejection with increasing molecular weight,<sup>14</sup> or number of constituent atoms.<sup>15</sup>

### 3.3.2 Ultrafiltration of Electrolytes

The problems associated with the ultrafiltration of electrolytes are much more complex than those associated with non-electrolytes. The simplifying assumptions of Manegold<sup>16</sup> as regards the lack of solute adsorption are of questionable applicability. In addition, the ability of ionic species in

general to hydrate water makes the accurate determination of Manegolds<sup>16</sup> "R" rather difficult.

Perhaps the most important single paper in the field of electrolyte ultrafiltration is the classic work of Reid and Breton<sup>17</sup> who studied the ultrafiltration of aqueous salt solutions through numerous membranes. The results of their studies are most conveniently described in tabular form as in Table 7.

Table 7

Membrane Selectivity Towards Aqueous Sodium Chloride

Membrane Tested	% Selectivity*
Polyvinyl Alcohol	26
Amberplex A-1	None
Amberplex C-1	None
Ethyl Cellulose	None
Nylon	None
Cellophane	6
Rubber Hydrochloride	No Flow
Polystyrene	None
Saran	None
Cellulose Acetate	96-97.4

$$*\% \text{ Selectivity} = \frac{[\text{Cl}]_{\text{feed}} - [\text{Cl}]_{\text{effluent}}}{[\text{Cl}]_{\text{feed}}} \times 100$$

Of the materials investigated, cellulose acetate was by far the most promising from the standpoint of sodium chloride rejection and was thus given additional study.

Of the many theories proposed for the phenomenon of semipermeability none really completely explains the greater water:electrolyte adsorption or solubility exhibited by cellulose acetate relative to polyvinyl alcohol or cellophane. Although the latter possess a large abundance of hydrophilic hydroxyl groups, these materials could not successfully reject NaCl.

Baker, Fuller, and Pape<sup>18</sup> showed that cellulose acetate was unique in possessing a moderate degree of crystallinity which would concurrently decrease the amount of Brownian movement allowable in the amorphous region of this material. Reid and Breton go on to postulate that the water which does accumulate in the amorphous regions of cellulose acetate is held by hydrogen bonding to the carbonyl oxygen and as a consequence of the smaller pore size is more tightly bound than in either cellophane or polyvinyl alcohol. The postulates of Reid and Breton are as follows:

(1) The reduced pore sizes in cellulose acetate are a consequence of increased crystallinity and more tightly bound water.

(2) Ions and molecules that cannot enter into hydrogen bonding are transported by hole type diffusion.

(3) Ions and molecules that can enter into hydrogen bonding and can fit into the bound water structure move by alternate alignment type diffusion, that is, by alternate hydrogen bond making and breaking until discharge is complete.

In line with the postulates above, Reid and Breton consider electrolyte rejection to be a direct consequence of reduced diffusion rate of ions through the "bound water" filled pores.

McKelvey, Spiegler, and Wyllie<sup>19</sup> studied ultrafiltration through ion-exchange-group-containing membrane filters and concluded that rejection was in accordance with the well established Donnan equilibria. The efficiencies of these membranes from the standpoints of flux and rejection are below those of cellulose acetate.

### 3.4 Analytical Methods

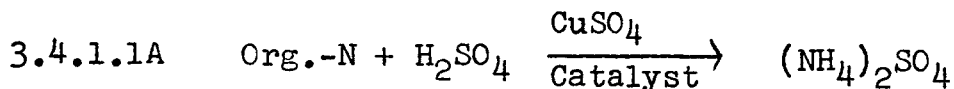
In view of the exploratory nature of the program, a need existed for good analytical methods for urine as well as product waters. For the sake of simplicity these are discussed under separate headings.

#### 3.4.1 Urea-Analysis

The most prominent contaminant present in human urine is urea. In view of the relatively high solubility of its salts and condensation products (in water) the available analytical methods entail conversion to ammonia via a hydrolytic reaction. Two prominent methods for ammonia analysis are the well known Kjeldahl<sup>20</sup> and the more recently developed Indophenol<sup>21</sup> techniques.

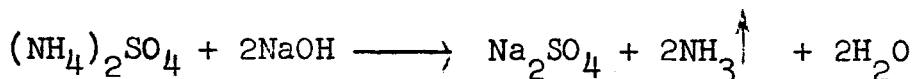
##### 3.4.1.1 Kjeldahl Method

The Kjeldahl method is used as a means of total organic nitrogen determination. In essence the process entails an acid catalyzed digestion with sulfuric acid in order to convert all organic nitrogen to ammonium sulfate via 3.4.1.1A.



The formed ammonium sulfate is then converted to free ammonia and distilled from the basic reaction medium via

3.4.1.1B below:

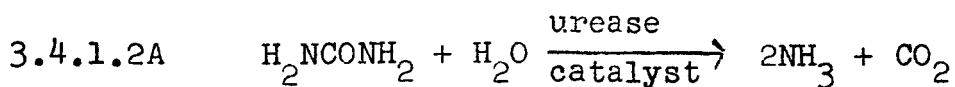


The ammonia distilled off is trapped in either dilute sulfuric or boric acids and back-titrated or directly titrated as the choice of trapping agent dictates.

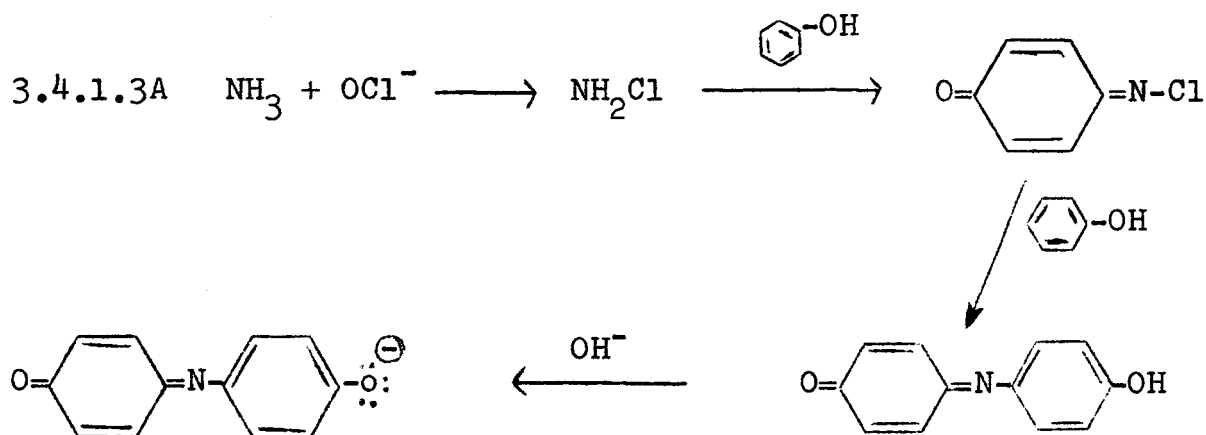
##### 3.4.1.2 Indophenol Method

The Indophenol method entails the urease catalyzed conversion of urea to ammonia and carbon dioxide as shown

in 3.4.1.2A below:



The liberated ammonia is reacted in situ with hypochlorite and phenol in an alkaline medium ultimately giving rise to the blue indophenoxide anion as depicted in 3.4.1.3A below.



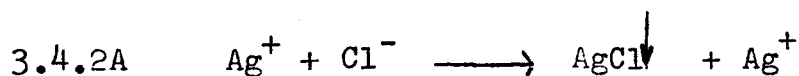
blue, abs. max. 6250 Å

Of the methods described above the Kjeldahl is more satisfactory from the standpoint of accuracy. The Indophenol method, however, has proved satisfactory for screening particularly in the area of synthetic urine specimens. In addition, the relative simplicity of the indophenol method has made it the method of choice for numerous experiments.

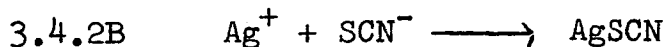
### 3.4.2 Chloride Ion-Analysis

The second most prominent contaminant present in human urine is the chloride ion. Due to its almost universal applicability, the Volhard method was used throughout the course of the program.<sup>22</sup>

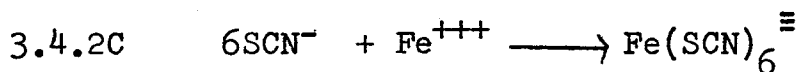
In this method the chloride-containing sample is titrated with an excess of standard silver nitrate solution as per 3.4.2A below:



the excess silver ion is then back-titrated with standard thiocyanate solution as per equation 3.4.2B.



the first drop of excess thiocyanate reacts with ferric alum indicator as indicated in 3.4.2C to give the colored ferrithiocyanate ion



soluble red-orange-brown

Nitrobenzene is added at the end of the silver nitrate titration to prevent the equilibration of thiocyanate ion with precipitated silver chloride via 3.4.2D which would give rise to abnormally high results



### 3.4.3 Solids-Analysis

The determination of solids is an extremely important measure of successful purification of a water supply. The determination of solids entails the drying of a sample of unit volume to constant weight at a given temperature. The U.S. Public Health Service specifies a definite maximum allowable solids concentration for a drinking water supply.

## 4.0 EXPERIMENTAL

### 4.1 The Ultrafiltration System

From a practical standpoint, ultrafiltration entails the impingement of a liquid under pressure against the surface of a membrane filter. Those species which are permeable traverse the membrane filter under a slight pressure and are then collected in a suitable container. Those materials which cannot permeate the membrane filter remain outside and are either recycled or discharged as desired. The experimental system was designed to allow for:

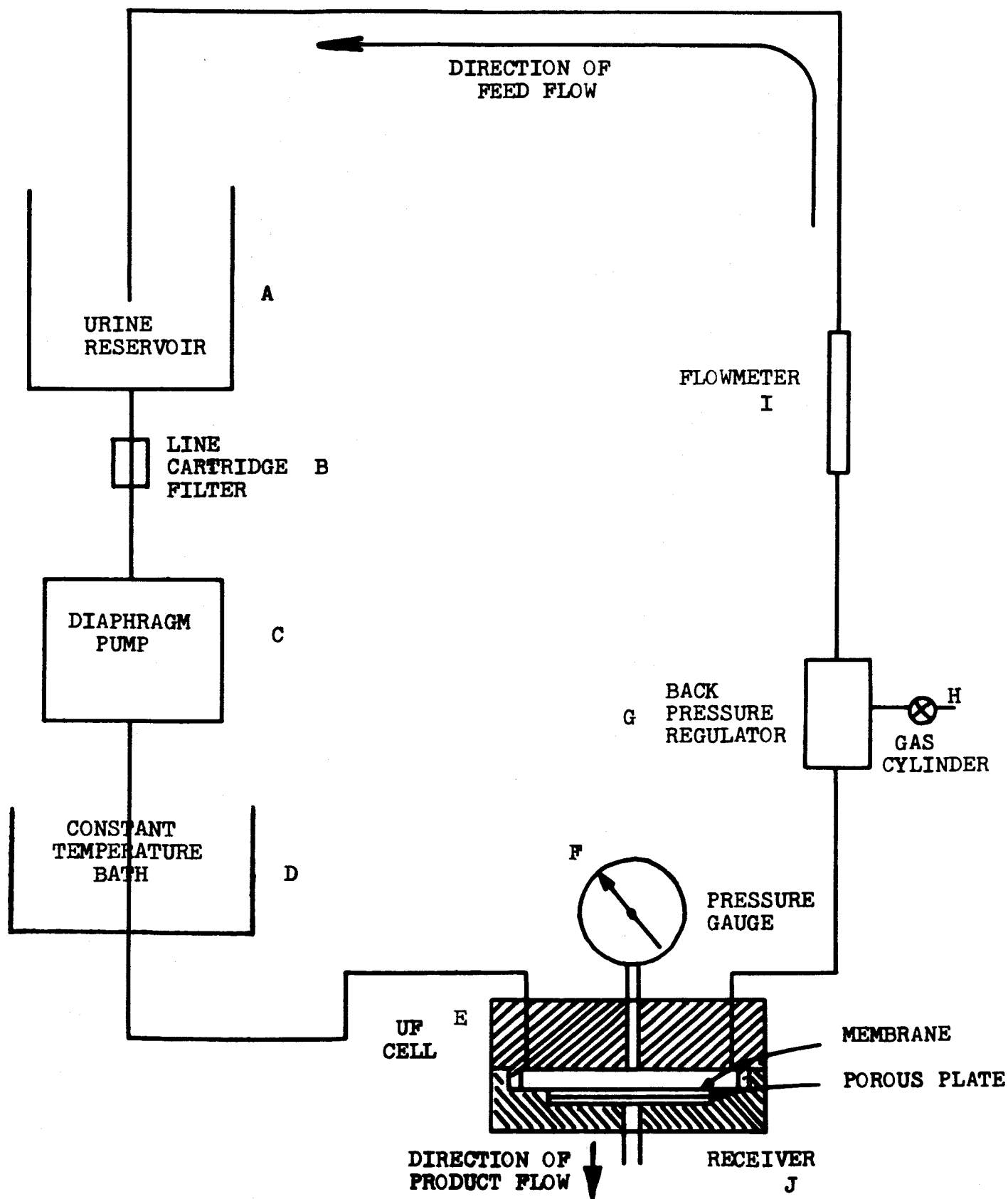
- a. ease of membrane interchange,
- b. study of superficial velocity effects by precise control of volumetric throughput,
- c. variation in operational pressure and temperature,
- d. optional discharge or recycle of feed stream.

A schematic diagram of the experimental system possessing the aforementioned facets is shown in Figure II.

In practice, the experimental system operated as follows:

Treated or un-treated urine was charged into the reservoir (A) and then passed through the line cartridge filter (B) where any stray particulate matter larger than  $10\mu$  was removed. The ultrafiltrand then was drawn into the diaphragm pump (C) where the pressure was increased from ambient to the 2000 psi level. The ultrafiltrand was then passed under pressure through the constant temperature bath (D) where the temperature could be raised or lowered as desired. The sensing probe for the constant temperature bath was placed in the ultrafiltrand stream in order to minimize the time lag. After leaving the constant temperature bath the ultrafiltrand was passed across the

FIGURE II EXPERIMENTAL ULTRAFILTRATION SYSTEM



filter paper-supported membrane in the ultrafiltration cell (E).

The cavity in the ultrafiltration cell was a 4-inch cylinder with a height of  $1/16$  inch. In operation, the top part of the cell was raised from the bottom by the sealing quad ring. This resulted in a cylindrical 4-inch diameter cavity having a height of ca.  $1/16$  inch.

The product water, having traversed the membrane passed through the supporting porous plate and was collected in the receiver (J). The unfiltered feed left the cell and passed through the back pressure regulator, (G), which was activated by a gas cylinder, (H). As a consequence, the liquid feed pressure was reduced to the near atmospheric level. The feed then passed through the flow meter, (I) and returned to the urine reservoir, (A) for recycling or discharge. The experimental ultrafiltration cell, itself, is shown disassembled and assembled in Figures III and IV, respectively. Samples of the reservoir and effluent were taken periodically to determine the efficacy of the process. The line filter (B) was water washed after each run.

#### 4.2 Preparation of Cellulose Acetate Membrane Filters

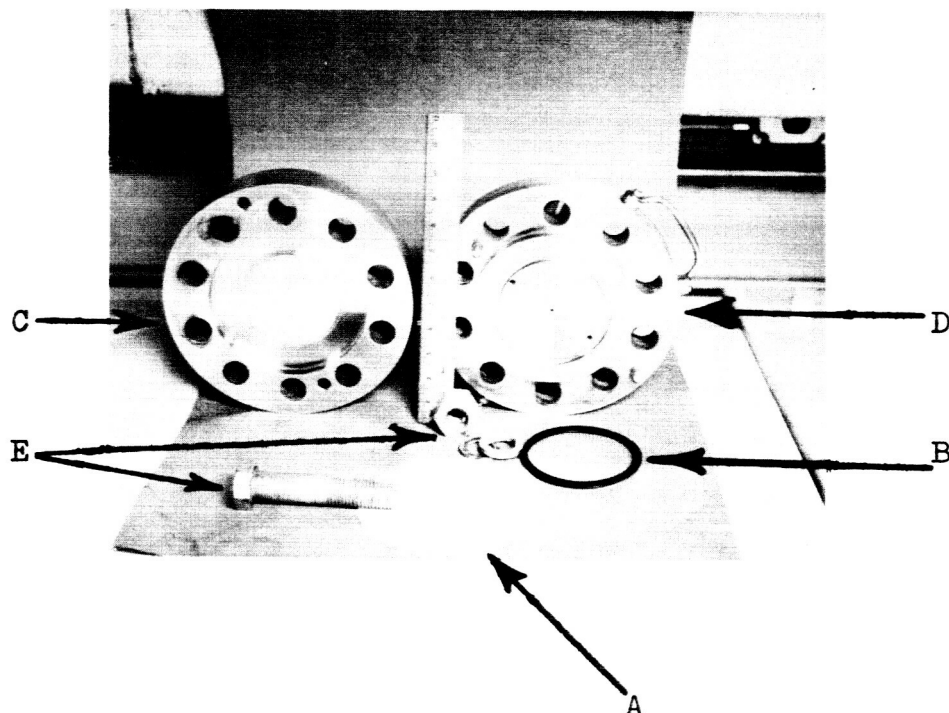
##### 4.2.1 The Casting Solution

The casting solution components used in the preparation of the membranes included the following:

- Cellulose Acetate (E 398-3) Eastman Kodak Co.
- Acetone
- Magnesium Perchlorate
- Water
- Hydrochloric Acid

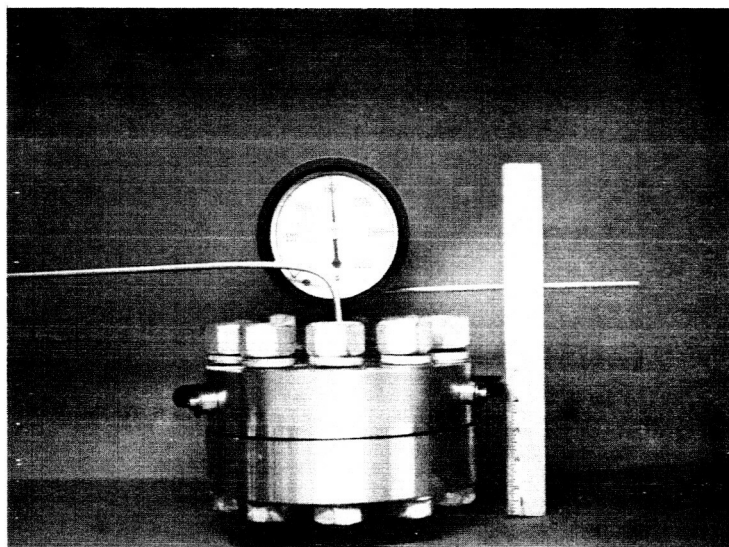
The ingredients were weighed into wide-mouthed, Teflon-gasketed bottles, closed, placed on a roll mill until solution was complete, and then cooled to an appropriate temperature.

FIGURE III Experimental Ultrafiltration Cell (Disassembled)



- A - Filter Paper Membrane Underlay
- B - Quad Ring
- C - Lower half of cell showing 3.73" diameter press fit stainless steel porous plate, sealing surface, and alignment pins.
- D - Upper half of Cell showing inlet and exit ports.
- E - (10)-1" diameter nuts, bolts, washers, and lock washers.

FIGURE IV Experimental Ultrafiltration Cell (Assembled)



Cell is shown bolted together. The feed and exit lines are also shown.

#### 4.2.2 Casting Procedure and the Quench Period

The cold casting solution was poured onto a cold glass plate and a doctor blade drawn across the plate. This left a wet film of uniform thickness on the glass plate. The plate containing the film was then placed in a cold environment for a time interval (the quench period) and then quickly immersed in an ice-water bath for 1 hour. The temperatures of the casting solution, glass plate, and cold environment during the quench interval and the length of the quench period are all important parameters in determining the properties of the membrane.

#### 4.2.3 Annealing Cycle

After the immersion in ice water, the film was peeled from the glass plate. It was subsequently placed in a circulating water bath which had been heated to the annealing temperature for a period of 20 minutes. At the end of this period the film was removed and placed in a bath of water at room temperature. The film was then considered ready for use. It is important that the side of the membrane facing the glass plate during the casting operation face the porous plate during the ultrafiltration operation.

Our work has involved a study of annealing temperatures from 75 to 90°C.

#### 4.3 Electrolytic Denitrification Compartment

The electrolytic denitrification used to remove nitrogenous matter from the urine is depicted in Figure V. In essence, the system consists of two closely spaced (to reduce resistance) porous platinum electrodes with a means of applying a DC potential across them. The DC potential can either be supplied by a 120 Volt AC house line coupled with a voltage

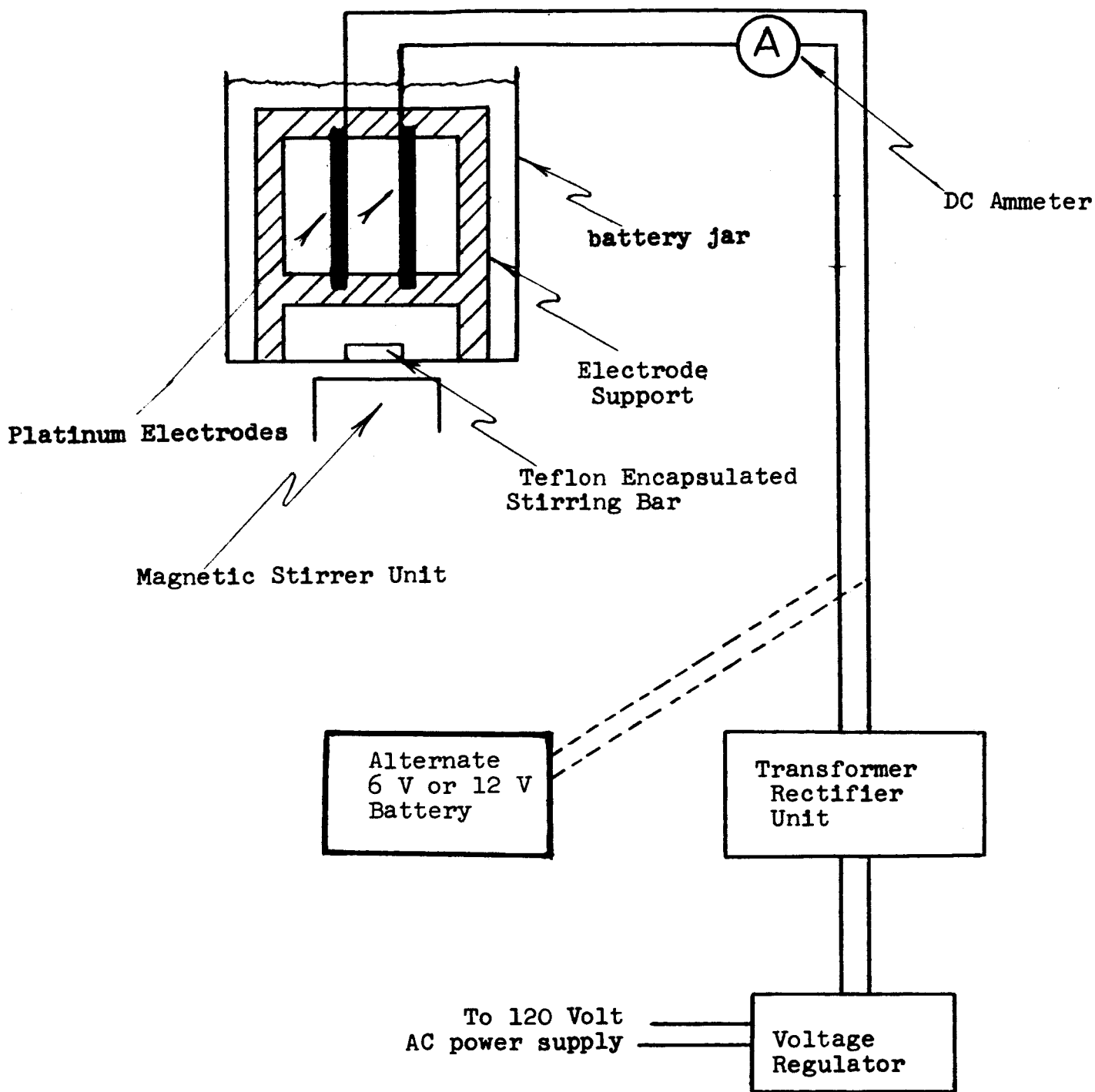


Figure V - Experimental Laboratory Electrolysis Unit

regulator-transformer rectifier combination or a standard 6V or 12 Volt battery.

In practice, the urine is charged into the battery jar, the stirrer turned on, and the potential applied. The minimum potential required is the "plating potential" of the chloride ion on the particular electrode of choice. With platinum, as with other electrodes, the overvoltage is dependent on the nature of the electrode surface. The electrolysis is continued until the urine is Kjeldahl-nitrogen-free.

#### 4.4 Analytical Procedures

##### 4.4.1 Chloride Ion-Volhard Method<sup>22</sup>

##### 4.4.1.1 Materials

a. Dilute Nitric Acid - (conc.  $\text{HNO}_3$ : $\text{H}_2\text{O}$  1:1)

b. N/100  $\text{AgNO}_3$  - 1.70 grams of  $\text{AgNO}_3$  are dissolved in 1 liter of water. The solution should be stored in the dark in amber bottles and should be standardized by titration against a N/100 chloride sample prepared by dissolving 0.5845 grams of reagent grade, oven dried ( $100^\circ\text{C}.$ ) sodium chloride in 1 liter of water.

c. N/100 KSCN - Approximately 0.97 grams of KSCN (potassium thiocyanate) are dissolved in a liter of water. This material is standardized against the silver nitrate solution.

d. Ferric Alum Indicator - A saturated water solution of ferric alum is prepared and filtered.

e. Nitrobenzene - A good reagent grade is employed.

##### 4.4.1.2 Method

To a 0.5 ml. aliquot of urine (or a 10 ml. aliquot of effluent) is added 1 ml. of the diluted nitric acid.

The resulting solution is heated to a boil for 1 minute and

externally cooled to room temperature. To the solution is added the 10 drops of ferric alum indicator. If the color of the indicator persists an additional 2 ml. of diluted nitric is added and the solution reboiled. When the acidity is such that the color no longer persists, 25 ml. of N/100 AgNO<sub>3</sub> are pipetted in with stirring. To the solution is then added 3 ml. of nitrobenzene and the heterogeneous mass back-titrated with N/100 potassium thiocyanate until the red-orange endpoint persists for at least 1 minute. If the back-titration requires less than 3 ml. of KSCN the experiment is repeated using 30 ml. of AgNO<sub>3</sub> solution.

#### 4.4.1.3 Calculation

$$\text{concentration of Cl}^{-} \text{ in mgs./liter} = \left[ \frac{(\text{ml. AgNO}_3)(N_{\text{AgNO}_3}) - (\text{ml. KSCN})(N_{\text{KSCN}})}{(\text{ml. of sample})} \right] \times 35,460.$$

#### 4.4.1.4 Comment

Normal urine is approximately 0.10 to 0.20 molar in chloride ion (3546 to 7092 mgs./liter).

#### 4.4.2 Total (Urea + Ammonia) Ammonia-Indophenol Method<sup>21</sup>

##### 4.4.2.1 Materials

a. Urease-glycerol extract - This material is available from Long Island Surgical Supply Co. and should be refrigerated when not in use. The activity should be checked periodically using standard urea solutions.

b. Acetate buffer - 15 grams of sodium acetate are dissolved in 30 cc. of H<sub>2</sub>O, 10 ml. of glacial acetic acid added and then sufficient water to yield 100 ml. of solution.

c. Indophenol Test Solution # 1 - To 10.0 grams of phenol and 0.050 grams of sodium nitroprusside are added sufficient  $H_2O$  to make 1 liter. Store in amber bottle and refrigerate. This reagent must be prepared fresh monthly.

d. Indophenol Test Solution # 2 - To 5.0 grams of sodium hydroxide and 8.0 grams of commercial (5.25% bleach (sodium hypochlorite) is added sufficient water to make 1 liter. This reagent likewise is stored in an amber bottle, refrigerated when not in use, and prepared fresh monthly.

e. Colorimeter

f. Ammonium Chloride - 3.141 grams of dry ammonium chloride (dried at  $100^{\circ}C.$ ) are dissolved in 1 liter of water. This solution contains 1000 mgs. of  $NH_3$  per liter and is used in dilutions of 2/1000 and 5/1000 for the daily indophenol calibration curve.

g. Urea - 1.763 grams of dry urea (dried at  $100^{\circ}C.$ ) are dissolved in 1 liter of water. This solution contains the equivalent of 1000 mgs. of  $NH_3$  per liter and is used in dilutions of 2/1000 and 5/1000 for the daily indophenol calibration curve.

#### 4.4.2.2 Method

(a) Dilution of Sample

1/2 ml. aliquot of urine (or feed) solution is diluted to 1 liter with deionized water. An effluent sample is diluted from 1 to 3 ml. per 100 ml. with deionized water.

(b) Conversion to Ammonia

A 1 ml. aliquot of the diluted sample from f. is carefully pipetted into a 10 ml. volumetric flask. To the aliquot are added 1 drop of urease and 2 drops of acetate buffer. The flask is carefully rotated to insure complete mixing of

the reagents and then allowed to stand for 1 hour. The diluted standard solutions are used as standards for each analytical series.

(c) Conversion to Indophenol

At the end of the aforementioned period 4 ml. each of Indophenol Test Solutions # 1 and # 2 are pipetted into the 10 ml. volumetric flask followed by sufficient  $H_2O$  to bring to the 10 ml. mark. The solution is allowed to stand a minimum of one hour, poured into the "spectronic 20" test tube and the Optical Density measured against the blank consisting of all the additives but the  $NH_3$  containing sample. After an additional 15-30 minutes the OD's are again read versus the blank to insure that all the colors are completely developed.

NOTE: The O.D. of any sample should fall between 0.2 and 0.8 and all more intensely developed solutions should be diluted accordingly and the OD's of the diluted samples determined. When working with urea containing solutions dilute the standard urea solution 2/1000 and 5/1000 and proceed as per (b). When using ammonia solutions (urea-free) the need for urease digestion is eliminated and the addition of urease and acetate buffer is eliminated (the 1 ml. aliquot is pipetted into the 10 ml. volumetric flask and one goes on directly to step (c) from there). In the latter case the ammonium chloride standard is diluted 2:1000 and 5:1000 for calibration purposes.

(d) Calculation

A plot of  $[NH_3]$  vs. optical density is made and from the slope ( $[NH_3]$  per OD unit) the concentration of the ammonia in the diluted aliquots is calculated. These figures are then multiplied by the dilution factor to arrive at the

concentration of ammonia in a given sample.

#### 4.4.3 Total Solids

##### 4.4.3.1 Materials

- a. Aluminum Cups - 30 ml. capacity weighing 1-2 grams
- b. Constant Temperature Oven -  $100 \pm 5^{\circ}\text{C}$ .

##### 4.4.3.2 Method

An aluminum cup is accurately weighed on the analytical balance to the nearest 0.1 milligram. An effluent aliquot (ca. 25 ml.) is pipetted into the cup. The cup plus effluent are placed in the oven set at  $100^{\circ}\text{C}$ . and dried until the loss in weight per 24 hour period is less than 0.6 milligrams. This is considered the final weight.

##### 4.4.3.3 Calculation

$$\begin{array}{l} \text{Solids} \\ \text{Concentration} \\ \text{in} \\ \text{milligrams/liter} \\ \text{(parts per million)} \end{array} = \frac{(\text{Final Weight Cup} - \text{Initial Weight Cup})1000}{\text{Volume of Effluent Aliquot in ml.}}$$

## 5.0 RESULTS AND DISCUSSION

The subject program was subdivided into the three distinct though strongly inter-related areas indicated below:

- I Membrane Development Program
- II Urine Treatment Program
- III Ultrafiltration Parametric Study

The prime purpose of subdividing was to allow for individual development in each area in the shortest possible period without the creation of a "lag time" between phases. For the purposes of clarity, each area will be given individual attention.

### 5.1 The Membrane Development Program

Key to the successful ultrafiltration approach to potable water recovery lies in the fabrication of membrane filters capable of high level solute rejection with concurrent high level water transmission.

#### 5.1.1 Commercially Available Membrane Filters

As a first approach it was decided to evaluate commercially available films as possible membrane filters in order to choose a substance of maximum promise for further development. To still further simplify the screening process, synthetic urine specimens consisting of urea and sodium chloride at concentration levels equivalent to those normally found in human urine were employed. This has the additional advantage of providing a constant concentration feed in contrast to the compositional variance found in normal urine. The results of these studies are summarized in Table 8.

Table 8

Commercial Films as Membrane Filters in Synthetic Urine Ultra-filtration at 2000 pounds/sq. inch Pressure

Expt. No.	Membrane	Water Flux, $\phi$ , in lbs./ft. <sup>2</sup> /hr.	% Rejection* in	
			$\overline{[Cl^-]}$	$\overline{[Urea]}$
10	Polyethylene Terephthalate	no flow	-	-
47L	66 Nylon	no flow	-	-
88A	Cellophane	1.51	21	9
88B	Cellophane	1.39	20	7
88C	Cellophane	1.51	21	7
89B	Cellulose Acetate	0.05	99.9	36
134A	Cellulose triacetate	2.23	87	37

$$*\% \text{ Rejection} = \frac{\overline{[Species]}_{\text{Feed}} - \overline{[Species]}_{\text{Effluent}}}{\overline{[Species]}_{\text{Feed}}} \times 100$$

Of the materials tested the relatively hydrophobic species polyethylene terephthalate and 66 Nylon failed to allow any water transmission under a 2000 psi head. Commercial cellophanes (88A, B, C) demonstrated reasonable fluxes though poor  $Cl^-$  and extremely poor urea semipermeability. Cellulose acetate and triacetate looked extremely promising from the standpoint of chloride ion rejection and the former was ultimately chosen for further fabrication studies.

#### 5.1.2 Ion-Exchange Membrane Filters

In view of RAI's position as a fabricator of ion exchange group containing membranes, it was decided to evaluate these materials as membrane filters in the ultrafiltration cell. The results of these studies are recorded in Table 9.

Table 9

Ultrafiltration of Synthetic Urine through Permion Membrane Filters  
at 2000 psi

Expt. No.	Membrane	Water Flux, $\phi$ , in	% Rejection	
		lbs./ft. <sup>2</sup> /hr.	[Cl] <sup>-</sup> in	[Urea]
91A	Permion 1000	0.08	96	59
91C	Permion 910	0.26	95	41
92A	Permion 202	1.15	60	60
93B	Permion 102	0.23	65	27

Although the chloride ion rejections exhibited by Permion 1000 and Permion 910 are relatively high, the relatively poor fluxes (and low urea rejections) negated against these species.

In view of the results obtained with commercially available films (including ion-exchange types) it was decided to further develop the cellulose acetate membrane filter in view of its demonstrated 99.9% sodium chloride rejection.

5.1.3 Cellulose Acetate Membrane Filters

Preliminary screening studies with commercially available films pointed toward cellulose acetate as the most promising material of fabrication for membrane filters. Thus, the bulk of the program was directed toward increasing flux while maintaining high level of rejection towards this species.

The membrane filter characteristics of cellulose acetate can be markedly varied by alteration of the film fabrication parameters. Among the many variables in film fabrication, particular emphasis was placed on the following:

- a. Composition of the casting solution,
- b. temperature of the casting solution,
- c. quench interval between casting the film and immersing it in ice cold water,
- d. annealing temperature.

In view of the importance of these variables, they will be discussed on an individual basis.

#### 5.1.3.1 Casting Solution Composition

The effective use of casting solution additives as a means of bolstering flux characteristics without marked loss of semipermeability has been adequately demonstrated by Loeb.<sup>23</sup> Using a formulation consisting of cellulose acetate, acetone, and water, an entire series of salts and non-electrolytes were added and the effects on flux and rejection characteristics in ultrafiltration were studied. Of all the additives evaluated, the most promising membrane filters were prepared from formulations containing magnesium perchlorate,  $Mg(ClO_4)_2$ . Studies conducted in this laboratory confirmed the findings of Loeb and resulted in membrane filters of much higher porosity than normally found in cellulose acetate. Table 10 indicates the magnitude of flux differences to be garnered as a consequence of magnesium perchlorate incorporation in the casting solution.

Table 10

Flux Dependency upon Magnesium Perchlorate Level in Casting Solution

Expt. No.	Membrane	Water Flux, $\phi$ , in lbs./ft. <sup>2</sup> /hr.	% Rejection in	
			[Cl <sup>-</sup> ]	[Urea]
89B	Commercial Cellulose Acetate	0.05	99.9	36
43R	Cellulose Acetate - $Mg(ClO_4)_2$	0.37	98	83

Thus, as a comparison of results indicates, it is possible to achieve a 7-8 fold increase in flux as a consequence of  $\text{Mg}(\text{ClO}_4)_2$  incorporation in the casting solution.

Studies by Loeb<sup>23</sup> and co-workers indicate as optimum the casting solution composition indicated in Table 11.

Table 11

Casting Solution Composition of Optimized Membranes

Composition	Weight of Components in grams
Cellulose Acetate	44.20
Acetone	132.40
Water	19.88
Magnesium Perchlorate	3.32
Hydrogen Chloride	0.66
Total:	<u>200.46</u>

Studies in these laboratories verified the findings of Loeb and co-workers. After ascertaining the applicability of the aforementioned casting solution composition as a means of preparing good membrane filters no additional compositional variation was made.

The role of the magnesium perchlorate additive in the preparation of cellulose acetate membrane filters remains in doubt. Prior studies<sup>24</sup> indicate that upwards of 90% of the perchlorate is removed in the normal fabrication. In view of these findings it appears quite probable that the role of magnesium perchlorate is organizational in nature, that is, the primary role is one of maintaining a porous molecular geometry during the actual casting step.

5.1.3.2 Casting Temperature

The term "casting temperature" refers to the temperature of the casting solution, doctor blade, glass plate, and environs. Although the exact role this temperature plays in the deposition

of the film is unclear, the role is of extreme importance. Membrane filters cast at  $0^{\circ}\pm 2^{\circ}\text{C}$ . were found to possess relatively low flux characteristics irrespective of the quench interval. Assuming the low fluxes to be due to excessive crystallinity, the casting temperatures employed were reduced to  $-10^{\circ}\pm 3^{\circ}\text{C}$ . This lower temperature allowed for the fabrication of membranes of much higher flux characteristics.

A reasonable speculation regarding the role of the casting temperature may be made as follows: Inasmuch as the acetone solvent has a high vapor pressure at temperatures of the order of  $0^{\circ}\text{C}$ ., the rate of acetone evaporation is strongly temperature dependent in these temperature ranges. The rate of acetone evaporation is also directly proportional to the rate of "deposition" of cellulose acetate. The rate of deposition is related to the amorphous : crystalline characteristics of the cast film. Thus, the lower the temperature one employs (1) the lower the rate of acetone evaporation (2) the slower the "deposition" rate of film and finally (3) the greater the amorphous : crystalline regions in the deposited film. Qualitatively, the hypothesis is borne out by the greater fluxes attained through membranes cast at  $-10^{\circ}\text{C}$ . versus those cast at  $0^{\circ}\text{C}$ .

#### 5.1.3.3 Quench Interval

The term "quench interval" refers to the time period between drawing down the fresh film and inserting the film in an ice water bath. During this formative period the cellulose acetate changes from a viscous acetone solution to an integral film. In general, the greater the duration of the quench interval the lower the porosity upon solution ultrafiltration. The increased

porosity with short quench intervals is however accompanied by poorer rejection characteristics. To illustrate consider the data in Table 12 below:

Table 12

Effect of Quench Interval on Flux and Rejection

Expt. No.	Quench Interval	Flux lbs./ft. <sup>2</sup> /hr.	% Rejection Cl-
62A	0 (instantaneous)	2.07	89
62B	2 minutes	0.86	96
62C	4 minutes	0.61	97

From the experimental data one may draw a reasonable hypothesis regarding the role of quench interval. If one assumes (1) that cellulose acetate "crystallization" takes place during the quench period and (2) insertion of the freshly cast film freezes the crystalline : amorphous areas, increasing quench intervals should increase the degree of crystallinity. With increasing crystallinity the (1) flux should decrease and (2) the rejection increase. This qualitative rationale quite accurately describes the data on quench interval throughout the course of the program. Our studies to date indicate an optimum quench interval of 8 minutes at -12°C.

#### 5.1.3.4 Annealing Temperature

The temperature of the water bath in which the cellulose acetate membranes are heated is referred to as the "annealing temperature". During this annealing operation, a large degree of orientation is believed to take place in the cast films. The importance of this operation was historically demonstrated by Loeb<sup>23</sup> in studies on performance characteristics of cellulose acetate membrane filters in sea water ultrafiltration. These studies clearly indicated the need for annealing. In general,

increasing the annealing temperature (1) decreases the flux and (2) increases the ion rejection of cellulose acetate membrane filters. This tendency is adequately demonstrated by the data in Table 13.

Table 13

Membrane Characteristics as a Function of Annealing Temperature

Expt. No.	Annealing Temperature (°C.)	Flux lbs./ft. <sup>2</sup> /hr.	% Rejection Cl <sup>-</sup>
57A	78	2.32	91
57B	80	1.30	97
57C	82	1.04	97

In view of the decreasing flux and increasing semi-permeability accompanying increasing annealing temperature, a balance among the characteristics must be attained. Our studies indicate the desirability of annealing temperatures of the order of 88°C.

## 5.2 Urine Treatment

### 5.2.1 The Need for Pre-Treatment

Ultrafiltration studies conducted in this laboratory using a wide variety of membrane filters have repeatedly failed to uncover a membrane filter capable of directly rejecting urea species. The commercial cellulose acetate films which gave excellent salt rejections (99.9%) possessed extremely poor urea rejecting characteristics (36%). Multiple variations in the CA film fabricating parameters likewise gave repeatedly low level (less than 80%) urea rejections. The results of typical experiments in attempted urea rejection are shown in Table 14.

Table 14

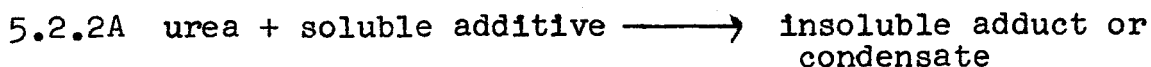
Characteristics of Cellulose Acetate Membrane Filters

Expt. No.	Flux lbs./ft. <sup>2</sup> /hr.	% Rejection	
		[Cl <sup>-</sup> ]	[Urea]
38	1.51	97	64
43L	1.24	98	72
73A	2.72	96	69
76A	0.31	97	74
80C	0.25	96	77

Although these membrane filters possess a degree of selectivity towards urea, the level is far from sufficient. Inasmuch as normal urine contains approximately 24,000 parts per million of urea, rejections of the order of 99% are required to reduce the urea solids in the product water to the 240 parts per million level. Note - The United States Public Health Service<sup>25</sup> specifies a 500 parts per million level as the maximum allowable solids concentration in a drinking water supply. In view of the repeatedly demonstrated inability of numerous membrane filters to give high level urea rejections, several alternative approaches were considered. These included (1) urea insolubilization via adduct or condensate formation, (2) conversion of urea to an ionic (filterable) species, and (3) electrolytic urea removal (denitrification). These approaches are discussed below under separate heading.

5.2.2 Attempts at Urea Insolubilization

A reasonable chemical approach to the problem of removing urea from urine entails the use of soluble additives to form insoluble urea adducts or condensates via a reaction of the type depicted in 5.2.2A below:



This approach would become even more attractive if one could regenerate the additive via some physical means. To achieve the aforementioned goal a series of additives including hydrochloric, nitric and oxalic acids, xanthhydrol, and formaldehyde were evaluated. All of these materials failed to effectively insolubilize urea for reasons delineated in Table 15.

Table 15

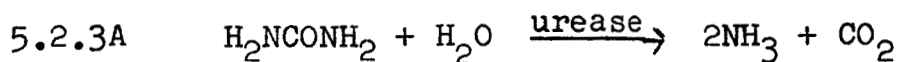
Attempted Urea Insolubilization via the Use of Additives

Additive	Expected Product	Reason for Failure
HCL	urea•HCL	Too soluble adduct
HNO <sub>3</sub>	urea•HNO <sub>3</sub>	Too soluble adduct
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (oxalic acid)	(urea) <sub>2</sub> •H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Too soluble adduct
Xanthhydrol	Dixanthhydryl urea	Xanthhydrol too insoluble
Formaldehyde	urea•Formaldehyde Condensate	Condensate too soluble

In view of the shortcomings delineated above, the emphasis in the treatment program was shifted toward converting urea into a filterable (ionic) species.

### 5.2.3 Urea Conversion

The failure to (1) directly reject urea and (2) successfully precipitate urea via methods mentioned in 5.2.2 led to approaches entailing hydrolysis of the urea species. One of the best known reactions of urea is its hydrolysis to ammonia and carbon dioxide. This reaction is specifically catalyzed by the enzyme urease as depicted in 5.2.3A below:



Typical results in the attempt to ultrafilter synthetic urines consisting of sodium chloride and ammonium carbonate at

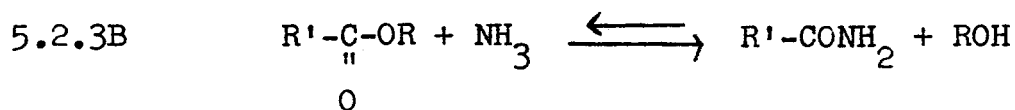
concentration levels equivalent to completely hydrolyzed real urine are shown in Table 16 below:

Table 16

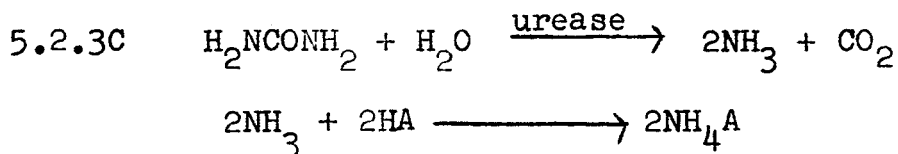
Ultrafiltration of NaCl,  $(\text{NH}_4)_2\text{CO}_3$  Synthetic Urine

Expt. No.	Flux lbs./ft. <sup>2</sup> /hr.	% rejection	
		$[\text{Cl}^-]$	$[\text{NH}_3]$
72B	1.02	95	78

The results clearly indicate the impracticality of urea hydrolysis as a sole means of improving the rejection quality of the cellulose acetate membrane filter. In addition, the possibility of membrane (cellulose acetate) degradation via ester-amide interchange<sup>26</sup> of the type depicted below:



negated the promise of this approach. In view of these shortcomings it was decided to convert the urea through ammonium carbonate to an ammonium salt via the sequence depicted in 5.2.3C below:



Among the host of acids (HA) one may select for ammonia acidification, our studies included acetic, hydrochloric, sulfuric, and citric because of their relatively low equivalent weights and diverse acidic character. The results of ultrafiltration studies on synthetic urine feed solutions containing these species are summarized in Table 17.

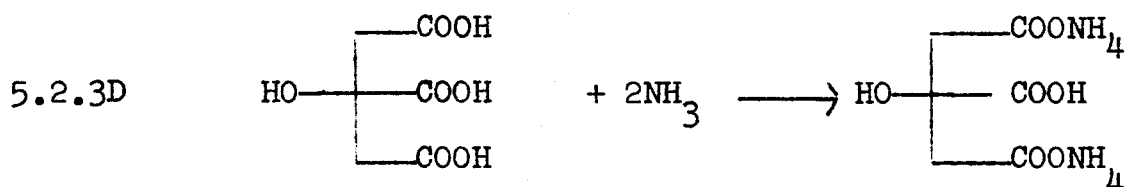
Table 17Ultrafiltration Studies on Synthetic Urines Containing  $\text{NH}_4^*\text{A}$ 

Expt. No.	$\text{NH}_4^*\text{A}$	% $\text{Cl}^-$ Rejection	% $\text{NH}_3$ Rejection
44L	$\text{NH}_4\text{Cl}$	96	94
44R	$\text{NH}_4\text{Cl}$	97	97
45L	$\text{NH}_4\text{OAc}$	94	95
45R	$\text{NH}_4\text{OAc}$	92	98
46L	$\text{NH}_4\text{OAc}$	95	95
46R	$\text{NH}_4\text{OAc}$	95	94
48L	$(\text{NH}_4)_2\text{SO}_4$	93	99
48R	$(\text{NH}_4)_2\text{SO}_4$	95	99
62B	Diammonium Citrate	96	99.3
62C	" "	97	99.3
63B	" "	94	95
65B	" "	95	98
66A	" "	97	99.3
66B	" "	97	99.4
67B	" "	96	99.4
67C	" "	97	99.3
69B	" "	96	99.1
69C	" "	93	99
71B	" "	97	99

\*

All Solutions were approximately 0.1 molar in  $\text{NaCl}$  and 0.8 molar in  $\text{NH}_4^+$

Referral to Table 17 indicates the feasibility of the conversion to an ionic species as a means of effectively "holding back" urea. The high level (94+%) semipermeability of cellulose acetate towards ammonium chloride, acetate, sulfate, and citrate were of a level never before achieved with equivalent concentrations of urea. Of particular interest were the studies conducted with diammonium citrate inasmuch as ammonium permeabilities of the order of 99+% were achieved. The use of citric acid as a neutralizing agent for the urease-generated ammonia is of extreme interest in view of its trifunctionality. The use of two of the three available acid hydrogens in citric acid for the purpose of acidifying is shown in equation 5.2.3D.



Thus, from a practical standpoint, the use of precise quantities of acid are not required inasmuch as (1) the use of excess amounts would be accounted for by additional mono-ammonium citrate formation and (2) the use of insufficient quantities would be accounted for by triammonium citrate.

The demonstrated capability of the cellulose acetate membrane filters to successfully reject ammonium salts in synthetic urine experimentation led us to impose equivalent conditions on real urine specimens and thus more realistically evaluate this approach. For this purpose a large urine specimen was collected and digested with catalytic amounts of urease at room temperature until conversion to ammonia was deemed complete. Based on the analytical ammonia determination, sufficient citric acid was added (1 mole per 2 moles of ammonia) to convert the

free ammonia-ammonium ion to diammonium citrate. The aforementioned acidification was accompanied by the evolution of copious amounts of carbon dioxide. The acidified urine (pH~5) was then charged into the ultrafiltration cell. The results of these experiments are presented in Table 18.

Table 18

Ultrafiltration of Real Urine  
(Urease digested - Citric Acid Acidified)

Expt. No.	Flux $\phi$ lbs./ft. <sup>2</sup> /hr.	% Rejection $\left[ \text{Cl}^- \right]$ $\left[ \text{NH}_3 \right]$		Solids (parts per million)
78A	0.86	97	99.2	340
78C	0.86	97	99.3	366
84A	1.24	98	99.2	390

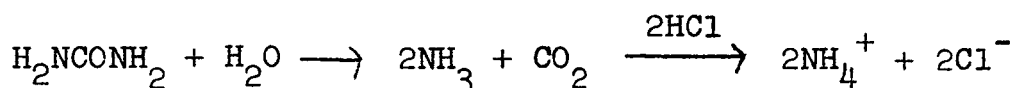
The results of these experiments are in line with those of the synthetic urine specimens as outlined in Table 17 and thus represented a possible route to potable water recovery via membrane ultrafiltration.

The ability of cellulose acetate membrane filters to reject ionic species more effectively than non-ionic species has repeatedly been demonstrated in this and other laboratories. The number of postulates to explain these results nearly equals the number of investigators in the field. Among the host of proposed mechanisms for rejection, negative absorption, steric considerations, and electrostatic repulsion are the most popular. Although the subject program was not designed to be definitive in nature, additional demonstration of high level ionic rejection has been demonstrated.

The primary problems associated with the conversion of urea, through ammonia, into an ammonium salt are (1) the need for stoichiometric quantities of an acid neutralizer for the

liberated ammonia and (2) the increased osmotic pressure of the feed solution with resultant depression of flux and attainable thermodynamic yield.

For a neutralizing acid with an arbitrary equivalent weight of 36 (hydrogen chloride) each liter of processed urine requires 36 grams to neutralize the urease generated ammonia. Multiplying by a composite factor composed of crew size and mission duration contributions, the use of additives at this level is contra-indicated. In addition to the aforementioned shortcoming, the conversion of urea through ammonia to an ammonium salt is accompanied by an increase in the osmotic pressure of the urine. Inasmuch as urea has a normal osmotic pressure contribution of 156 psi (see Table 3), the conversion of urea to an ammonium chloride, for instance, via the following sequence:



would give rise to a quadrupling of the osmotic contribution to  $4 \times 156 = 624$  psi. This treatment would, of course, markedly increase the magnitude of  $K_{\pi}$ , the gross retarding flux, and thus decrease the overall recovery rate,  $\phi$ , as per equation 3.1B.

With the limitations of the ammonium salt conversion process in mind, the experimental program was directed towards the removal of urea from urine via a technique which would not involve the use of additives. This end was attained through the "electrolytic" approach.

#### 5.2.4 Urine Electrolysis

Inasmuch as (1) urea permeates all known membranes suitable for water recovery and (2) the conversion of urea through ammonia to an ammonium salt is accompanied by excessive

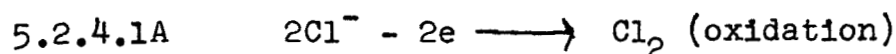
weight, flux, and yield penalties, the experimental program was directed toward a means of urea removal free of the limitations delineated above.

This goal was achieved via the subject electrolytic method as discussed in the ensuing section.

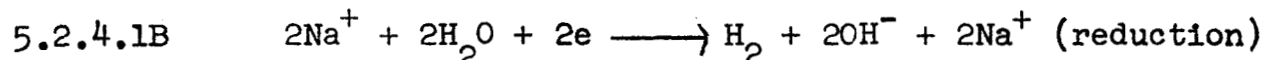
#### 5.2.4.1 Electrolysis of Salt-Urea Solutions

If one places a sodium chloride solution between inert electrodes and applies a sufficiently large DC potential, the following reactions can be made to take place at the electrodes indicated:

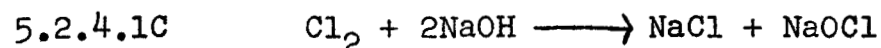
##### Anode



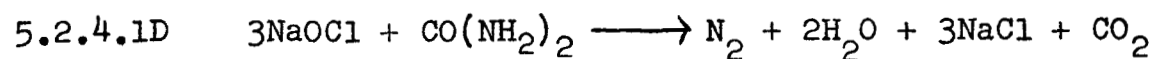
##### Cathode



If (1) the direct current density is kept sufficiently low, (2) the solution adequately stirred to prevent the discharge of chlorine, and (3) the gap between electrodes is kept sufficiently small so as to allow the chlorine formed at the anode to interact with the sodium hydroxide formed at the cathode, the following reaction, 5.2.4.1C may be made to take place:



The product sodium hypochlorite formed via the reaction above is a known<sup>8</sup> oxidant for urea and, as such, the electrolytic approach provides a method for the desired urea removal via conversion to nitrogen gas. The reaction is depicted below in equation 5.2.4.1D.



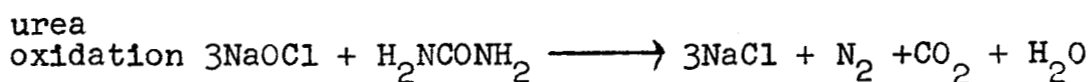
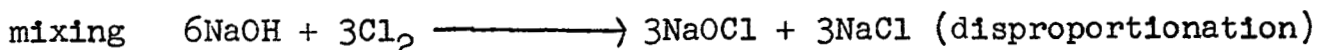
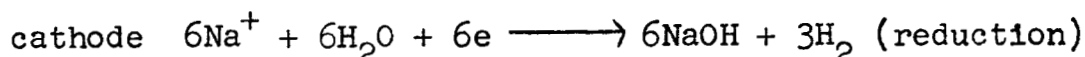
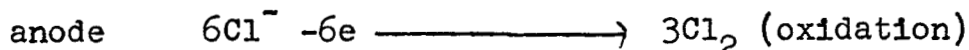
The spent sodium hypochlorite oxidant in its reduced form as

sodium chloride can conceivably be repetitively re-oxidized to sodium hypochlorite in order to provide sufficient oxidant to eliminate all the urea in the form of nitrogen gas.

#### 5.2.4.2 Electrolysis of Synthetic Urine

Preliminary experimentation in the electrolytic approach the urea removal was conducted with synthetic urine specimens consisting of urea and sodium chloride. In order to realistically determine the efficacy of the process, the synthetic urine was made 0.5 and 0.2 molar in urea and sodium chloride respectively. This concentration level closely approximates that in a real urine. For purposes of uniformity a series of electrolyses were conducted using 250 ml aliquots of the aforementioned urine. The theoretical rate of nitrogen disappearance in a 250 ml aliquot of the aforementioned synthetic urea solution at 0.5 amps was calculated via the sequence shown in 5.2.4.2A.

##### 5.2.4.2A Calculation of Theoretical Nitrogen Disappearance Rate



Thus, the oxidation of 1 mole of urea requires the passage of 6 Faradays in order generate sufficient NaOCl to satisfy the stoichiometry of the urea oxidation equation above. Thus, a 250 ml. aliquot of synthetic urine which is 0.5 molar in urea (14,008 mgs./liter of nitrogen as N) at an arbitrary 0.5 ampere electrolysis current should require a time, T,

$$T = \frac{0.5 \text{ moles urea}}{\text{liter}} \times 0.25 \text{ liters} \times \frac{6 \text{ Faradays}}{\text{mole urea}} \times \frac{96,500 \text{ Amp. Secs.}}{\text{Faraday}}$$

$$\times \frac{1}{0.5 \text{ Amps}} = 144,750 \text{ seconds} = 40.2 \text{ hours}$$

Therefore, the complete removal of urea nitrogen from a 250 ml aliquot containing 14,008 milligrams/liter of nitrogen as N should be accomplished at an average rate, R,

$$R = \frac{14,008 \text{ mgs. N/liter}}{40.2 \text{ hours}} = 348.4 \frac{\text{milligrams N}}{\text{liter-hr.}}$$

when operating at an arbitrary electrolysis current of 0.5 amperes.

In order to test the validity of the calculations in the 5.2.4.2A sequence, a series of experiments was conducted using a synthetic urine consisting of urea and sodium chloride at molar concentrations of 0.5 and 0.2 respectively. This solution was then electrolyzed using a platinum anode-carbon cathode at 0.5 amperes and aliquot samples removed periodically to determine the nitrogen concentration via the Kjeldahl method. The results are summarized in Table 19 and graphically depicted in Figure VI.

Table 19

Electrolysis of 250 ml. of Synthetic Urine at 0.5 Amperes

Sample #	Time (hrs.)	Nitrogen Concentration ( $\frac{\text{mgs. N}}{\text{liter}}$ )
78A	0	14,400
78B	12	10,500
78C	19	8,500
78D	35.5	2,100
78E	43.5	0

If one excludes the final sample 78E (inasmuch as the experiment cannot be stopped exactly at the zero nitrogen level) the process current efficiency, E, may be calculated via the expression 5.2.4.2B.

$$\begin{aligned}
 5.2.4.2B \quad E &= \frac{\text{actual nitrogen disappearance rate}}{\text{theoretical nitrogen disappearance rate}} \times 100 \\
 &= \frac{\frac{14,400 - 2,100 \text{ mgs. N/liter}}{35.5 \text{ hours}}}{348.4 \text{ mgs. N/liter - hour}} \times 100 = 99.4\%
 \end{aligned}$$

⊙ Nitrogen analysis via Kjeldahl method

PERS PER MILLION NITROGEN AS N

TIME IN HOURS

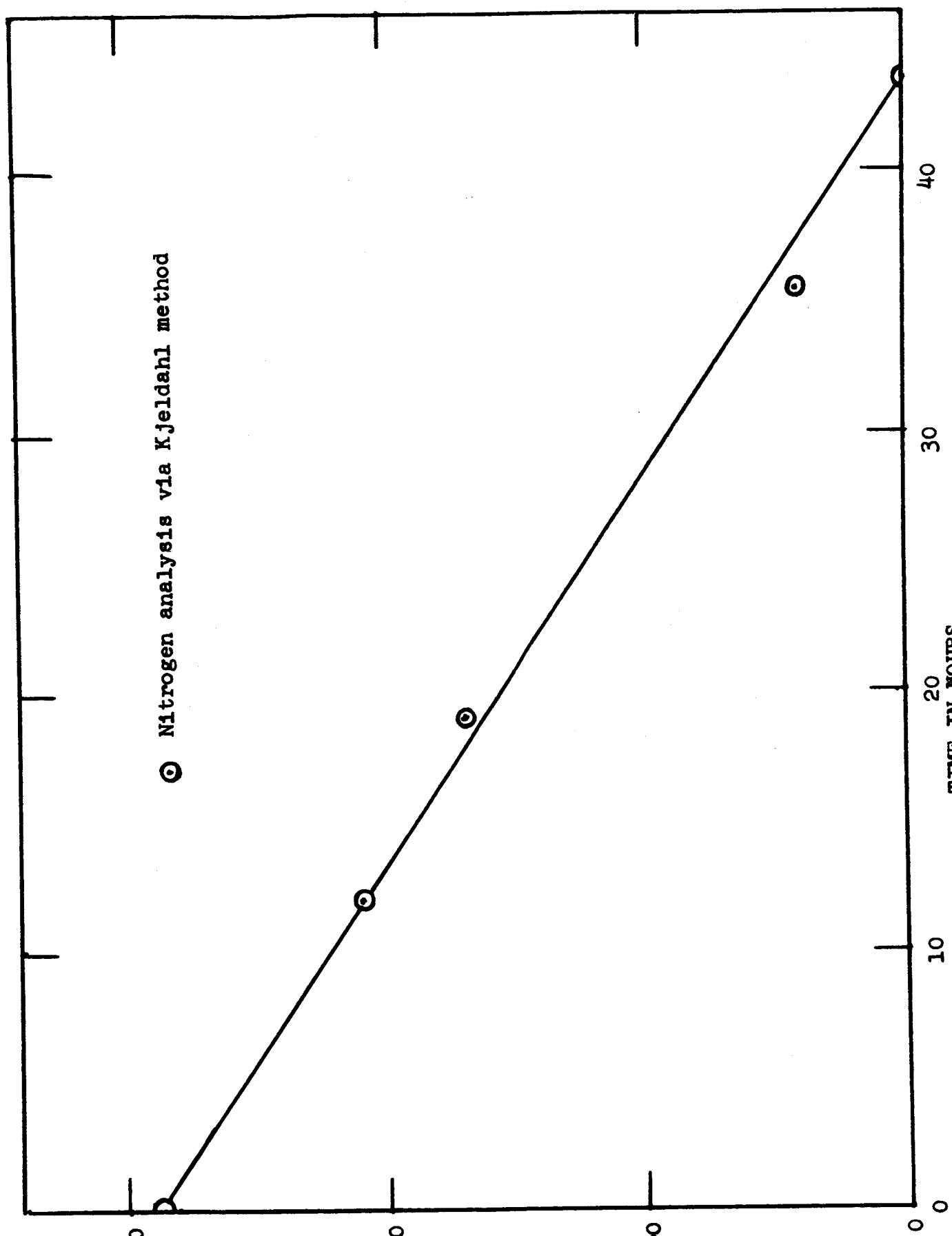
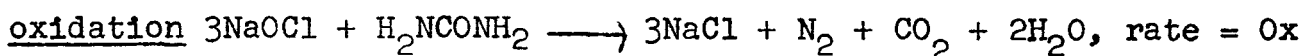
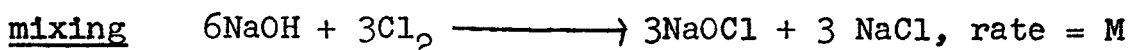
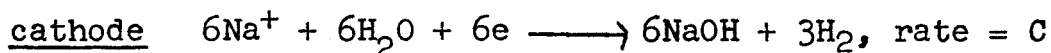
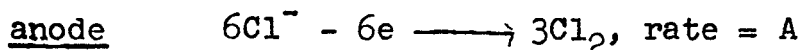


FIGURE VI Electrolysis of Synthetic Urine at 0.5 Amperes

The high level current efficiency achieved was a source of extreme interest and was considered a major breakthrough in the subject program. Considering the linearity of the curve in Figure VI, some reasonable assumptions regarding the process mechanism may be made. Assuming the reactions below to be the sole reactions occurring in the subject system



and the rates of the forward reactions are as indicated by the rate constants, the following assumptions may be made:

(1)  $A = C = \text{constant}$ , this is a consequence of Faraday's laws of electrolysis, that is the number of equivalents liberated at each electrode must be equal. The rates of these reactions, that is, the formation of chlorine and NaOH- $\text{H}_2$  are constant when conducting the electrolysis at a given fixed current. These rates were kept low in order to allow a preliminary study of the process kinetics. Under the experimental conditions imposed it is presumed that the rate of chlorine (or sodium hydroxide) formation are the slowest and thus rate determining for the process.

(2) The rate of mixing, M, of the evolved chlorine and sodium hydroxide to give rise to sodium hypochlorite is presumed to be relatively high and thus non-rate-controlling for the overall process. Excellent evidence for the rapidity of the aforementioned reaction exists in the ease of preparation of sodium hypochlorite from chlorine and sodium hydroxide at ice temperatures.<sup>28</sup>

(3) The rate of urea oxidation by hypochlorite,  $Ox$ , is believed to be extremely fast although no supporting kinetic evidence could be found in the literature. Preliminary experimentation in the titration of urea solutions with stoichiometric quantities of sodium hypochlorite solution (commercial bleach) indicate an extremely rapid gas evolution with resultant disappearance of nitrogen on post-analytical evaluation.

Intuitively then, the rate of the overall urea removal process rate is determined by the chlorine and sodium hydroxide liberation rates A and C respectively. Operation at higher reaction rates (current) could, however, change the picture.

#### 5.2.4.3 Electrolysis of Real Urine Specimens

The early successes attained with synthetic urine specimens (in terms of current efficiency) in urea removal directed the program toward the evaluation of the process in terms of urea removal in real urine specimens. To achieve this goal, urine specimens were collected among the male members of the laboratory staff and subjected to the electrolytic conditions described earlier (250 ml aliquots - 0.5 amperes).

The experimental results in rate of total nitrogen disappearance with time (milligrams N/liter-hour) as determined via Kjeldahl analysis are summarized in Table 20.

Table 20

Electrolysis of Synthetic and Real Urine Specimens  
(250 ml aliquots @ 0.5 amperes)

Expt. No.	Urine Specimen	Conc. of Nitrogen, N in mgs./liter		Electrolysis Time in Hrs.	Rate of Nitrogen Disappearance in mgs./liter-hr.
		original	final		
78	Synthetic	14,400	0	43.5	331
81	Real	18,100	16,200	41.0	46
87	Real	12,300	1,750	46.5	227
14	Real	12,110	2,275	42.3	233
15	Real	12,110	2,070	42.3	237
17	Real	11,370	2,240	41.5	220
18	Real	11,370	2,380	41.5	217
19	Real	11,370	1,100	41.5	247

Inasmuch as the theoretical rate of nitrogen disappearance for a 250 ml aliquot at 0.5 amperes is 348.4 milligrams of nitrogen per liter-hour, the current efficiencies achieved with real urine specimens were noted to be about 60% of those achieved with synthetic urine.

To offset this depleted level of current efficiency as measured by the Kjeldahl nitrogen depletion rate, a series of experiments was conducted using known oxidants (at the milligram concentration level) as electrolytic additives. The results of these experiments are shown in Table 21.

As the results indicate the addition of 10 milligrams of potassium permanganate increased the current efficiency to 78%.

A series of additives and/or pretreatments as indicated in Table 22 were evaluated.

Referral to the results in Table 22 point to the following:

(1) The efficiency of urea oxidation is independent of slight variations in acid and base strength.

(2) Although the urea-like cyclic intermediates uric acid, hippuric acid, and creatinine are prone to hypochlorite oxidation, the efficiency of these reactions appear somewhat lower than for urea.

(3) Irradiation of real urine aids the hypochlorite oxidation though no mechanistic explanation is as yet available.

(4) Pre-conversion of urea with urease into ammonium carbonate does not offer any aid to the denitrification process.

Table 21

Electrolysis of Real Urine Using Electrolytic Additives  
(250 ml aliquots @ 0.5 amperes)

Expt. No.	Additive	Conc. of Nitrogen, N in mgs/liter		Electrolysis Time in Hrs.	Rate of Nitrogen Disappearance in mgs/liter-hr.
		Original	Final		
82	CuSO <sub>4</sub>	13,500	4,500	45.0	200
83	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	10,300	3,100	40.0	180
85	H <sub>2</sub> O <sub>2</sub>	12,500	7,300	41.0	127
89	KMnO <sub>4</sub> (1 mg.)	10,800	100	89.5	111
5	HNO <sub>3</sub>	16,070	4,840	43.0	261
6	KMnO <sub>4</sub> (10 mg.)	16,430	4,720	43.0	272
7	HClO <sub>4</sub>	10,960	640	42.2	244

Table 22  
Effect of Other Treatments on Urine Electrolysis  
(250 ml aliquot @ 0.5 amperes)

Expt. No.	Additive and/or Treatment	Conc. of Nitrogen, N in mgs/liter		Electrolysis Time in Hrs.	Rate of Nitrogen Disappearance in mgs/liter-hr.
		Original	Final		
3	Urease Treated*	10,080	3,160	43.3	160
8	H <sub>2</sub> SO <sub>4</sub>	12,110	5,370	40.5	166
10	KOH	12,110	3,970	40.5	201
14	-	12,110	2,275	42.3	233
2	Irradiated 1.8 Mrads	15,920	1,390	47.3	307
38	Irradiated 2.0 Mrads	12,490	35	46.5	268
39	Irradiated 2.0 Mrads	12,490	710	46.5	253
57	Aerated	13,110	1,730	40.0	285
58	Charcoal Treated	12,180	1,310	40.0	272
32	Synthetic** Urine Plus	15,160	4,080	41.0	270
33	Synthetic** Urine Plus	15,160	3,220	41.0	291

\* Urease treatment was prolonged to the point where  $H_2O + H_2NCONH_2 \longrightarrow 2NH_3 + CO_2$  deemed complete.  
 \*\* Solution made 0.5 molar in urea and uric acid, hippuric acid, and creatinine added at typical urine concentration levels.

A large batch (11 liters) of nitrogen-free (as determined via Kjeldahl analysis) urine was prepared for the purpose of ultrafiltration study. The rate of electrolytic denitrification for the large batch is depicted graphically in Figure VII. It must be noted that the electrolysis indicated was conducted at an arbitrary 6 amperes. The calculated current efficiency of the large urine run is below that achieved with synthetic urine.

The following results and preliminary conclusions on the electrolysis of real urine have been reached:

(1) Electrolytic treatment provides a means of removing all nitrogenous matter present in human urine without recourse to the use of chemical additives.

(2) The electrolysis of urine is accompanied by a reduction in the bacterial count to below detectable levels.

(3) The ultrafiltered electrolyzed urine was free of pyrogens.

The conclusions (2) and (3) above are supported by an independent laboratory determination<sup>29</sup> and are included as Table 23. No attempt was made to identify the microorganisms from the membrane wash. The microorganisms present are due to contamination; they were not introduced in a controlled fashion.

(4) The theoretical power requirement is that required to produce sufficient hypochlorite to oxidize the urea. The calculated theoretical power requirement is shown in Table 24.

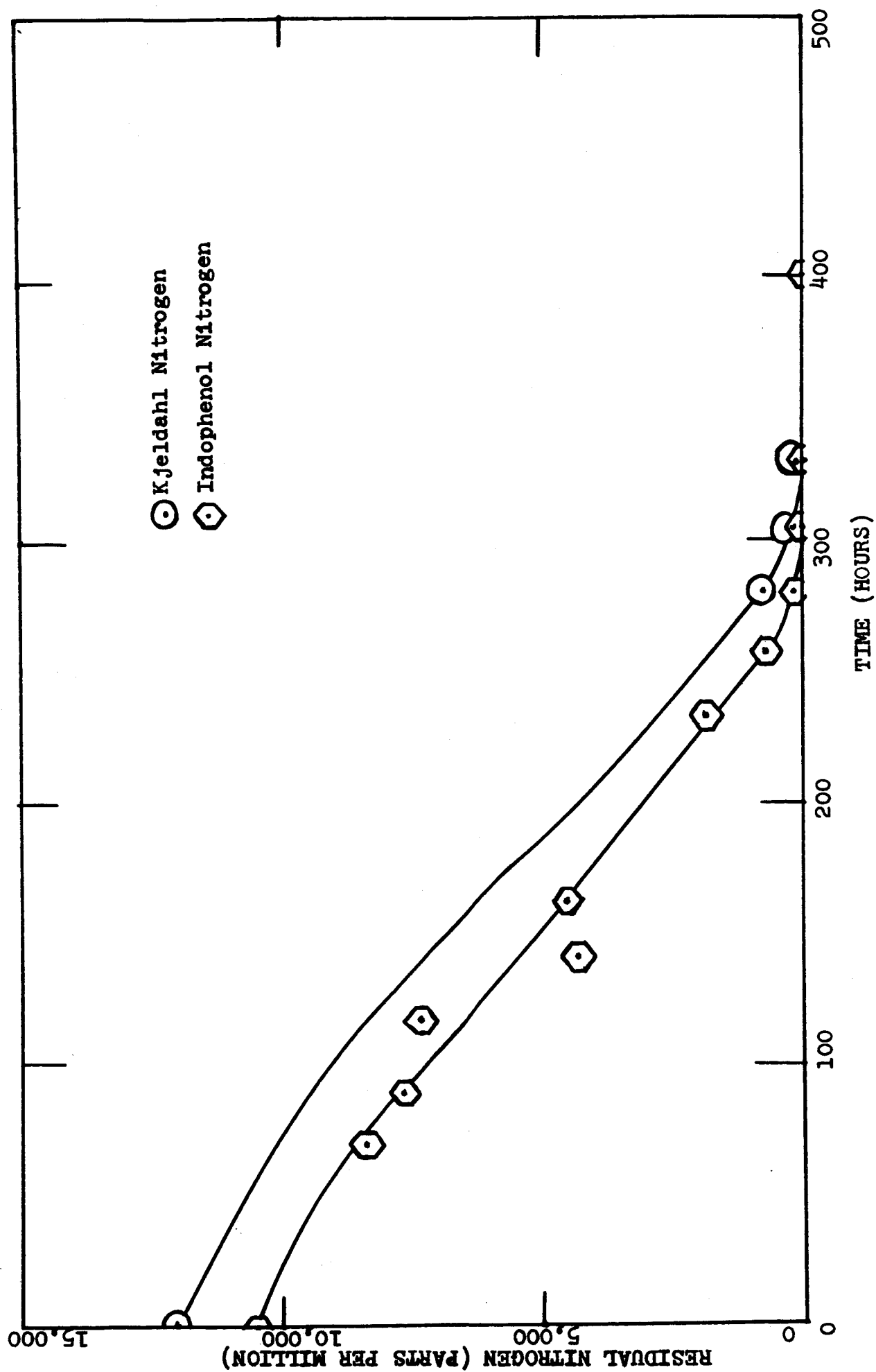


FIGURE VII Denitrification of Urine by Electrolysis (Large Batch Test)

Table 23

Total Bacteriological Count\*

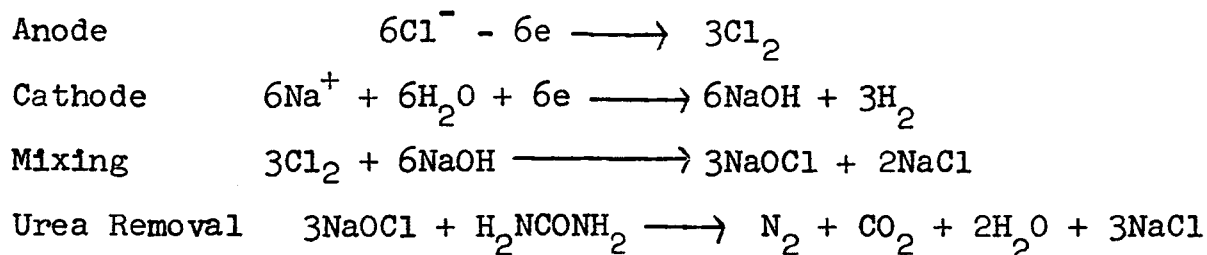
<u>Sample Identification</u>		<u>Total Bacteriological Count per ml</u>
<u>Laboratory</u>	<u>Markings</u>	
<u>No.</u>		
85240c	Membrane wash	9,900,000
85240a	"Sample No. 1 As Electrolyzed"	less than 5
85240b	"Sample No. 2 As Electrolyzed & Ultrafiltered"	less than 5

\*

"Standard Methods for the Examination of Dairy Products",  
11th Ed. (1960), p. 47.

Table 24

Theoretical Power Considerations in Urine Electrolysis



Thus, the oxidation of 1 gram-mole of urea requires 6 Faradays . Considering three astronauts, the total urine excretion to be expected per day = 4.5 liters, the urine to contain approximately 0.5 moles per liter of urea.

$$\begin{array}{l} \# \text{ of Faradays} = \frac{6 \text{ Faradays}}{\text{mole urea}} \cdot \frac{0.5 \text{ moles urea}}{\text{liter}} \cdot 4.5 \text{ liters} = 13.5 \text{ Faradays} \\ \text{required to} \\ \text{process three} \\ \text{astronauts} \\ \text{daily urine} \end{array}$$

Consider the Standard Oxidation Potential of  $\text{Cl}_2$  as 1.358 Volts,<sup>30</sup>  
the continuous power requirement, P,

$$\begin{aligned} &= 13.5 \text{ Faraday} \cdot \frac{96,500 \text{ Ampere-Seconds}}{\text{Faraday}} \cdot \frac{1 \text{ Day}}{86,400 \text{ seconds}} \cdot 1.358 \text{ V} \\ &= 20.4 \text{ watts/9.9 lbs. of urine processed each day.} \end{aligned}$$

## 5.3 Ultrafiltration Parametric Studies

### 5.3.1 Defining Equation

In the studies to be discussed a phenomenological description of the ultrafiltration process has been employed,<sup>2</sup> viz.,

$$5.3.1A \quad \phi = K(P - \pi')$$

where  $\phi$ : flux (lb. ft.<sup>-2</sup> hr.<sup>-1</sup>)

K: membrane transmission factor  
(lb. ft.<sup>-2</sup> hr.<sup>-1</sup> atm.<sup>-1</sup>)

P: operating pressure (atm.)

$\pi'$ : osmotic pressure at the membrane-ultrafiltrand interface (atm.)

The relationship shown in 5.3.1A is analogous to Ohm's Law where the flux,  $\phi$ , corresponds to current, the membrane factor, K, to conductance, and the pressure difference,  $P - \pi'$ , to the potential.

When the ultrafiltration process is employed to reclaim water from a finite volume of solution, the solute concentration in the residual solution increases with a concomitant increase in the bulk osmotic pressure. This causes an increase in the boundary-layer osmotic pressure with a resultant diminution of the driving force, i.e., the pressure difference,  $P - \pi'$ . This is evidenced by a decrease in the product flux,  $\phi$ .

Elimination of the osmotic pressure term in 5.3.1A, through the use of distilled water as the ultrafiltrand, permits evaluation of membrane transmission factor, K. Subsequent charging of the system with a solution having a bulk osmotic pressure,  $\pi$ , permits evaluation of the osmotic pressure at the membrane-ultrafiltrand interface,  $\pi'$ . The ratio,  $\pi'/\pi$  is an important design parameter, and as a consequence, its dependence on ultrafiltrand superficial velocity and concentration, and the membrane transmission factor, constitutes an area requiring investigation.

### 5.3.2 Membrane Compaction

The subjection of a given membrane to an elevated operating pressure is accompanied by a diminution in flux with time until an equilibrium is achieved between force resulting from the applied pressure and opposing tensile forces. It is imperative to achieve this equilibrium prior to the evaluation of membrane transmission factors.

#### 5.3.2.1 Time Dependence

The pressure on the cellulose acetate membrane causes compaction and a decrease in water transmission. This is demonstrated in Figure VIII which presents plots of flux in  $\text{lb.ft.}^{-2}\text{hr.}^{-1}$  versus operating time in hours.

Table 25

#### Membrane Compaction Study

Membrane	$\phi(\text{lb.ft.}^{-2}\text{hr.}^{-1})$		P(atm.)	$K(\text{lb.ft.}^{-2}\text{hr.}^{-1}\text{atm.}^{-1})$
	Initial	Equilibrium		
A	5.78	3.02	147	.0205
B	5.82	3.13	146	.0214
C	4.85	2.38	147	.0162

Inspection of Figure VIII will reveal that approximately 50 hours were required for an equilibrium flux value to be attained. In addition, it may be seen that the equilibrium flux is approximately one-half the initial value. It should be emphasized, however, that the time required to attain equilibrium and the ratio of equilibrium to initial flux vary between individual membranes.

A similar membrane compaction study was conducted using a 0.2M NaCl solution as the ultrafiltrand in order to observe simultaneously the effect of compaction on flux transmission and ionic solute rejection.

FIGURE VIII Ultrafiltrate Flux as a Function of Operating Time

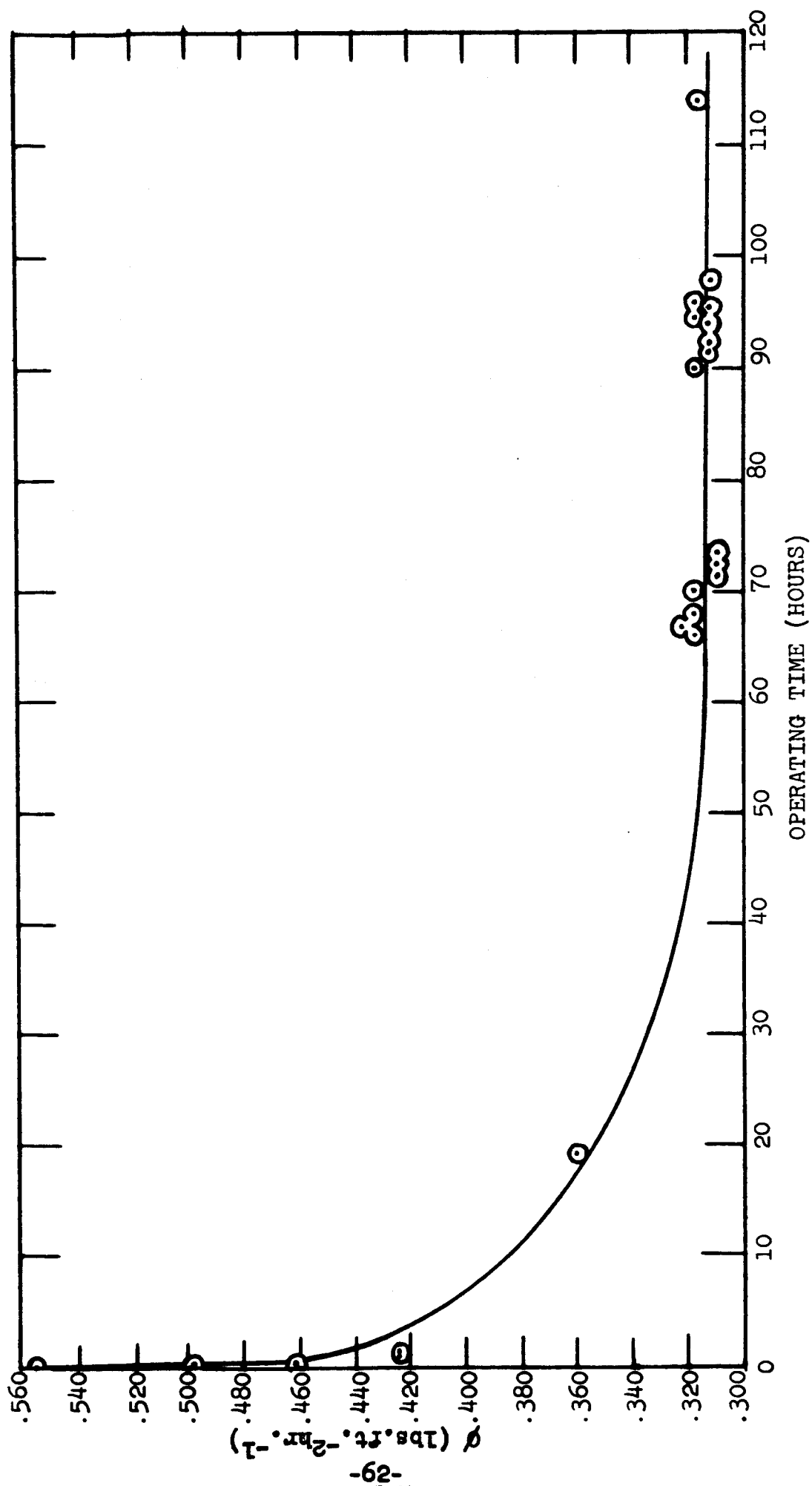


Table 26 and Figures IX and X present the data obtained.

Table 26

Membrane Compaction Study using an Ionic Solute

Elapsed Time (hrs.)	Ultrafiltrand Concentration (gm.-moles l. <sup>-1</sup> )	Flux (lbs.ft. <sup>-2</sup> hr. <sup>-1</sup> )	Ultrafiltrate Concentration (gm.-moles l. <sup>-1</sup> )x10 <sup>3</sup>
0.3	.2062	2.95	5.094
6.8	--	2.20	3.039
16.6	.2069	2.16	2.414
24.2	--	2.14	2.315
39.9	.2074	2.10	2.263

Figure IX constitutes a plot of flux versus elapsed time. The behavior of this curve is analogous to that obtained using a distilled water ultrafiltrand (ref. Figure VIII). Differences in compaction times are due to differences in the membranes employed.

Figure X is a plot of ultrafiltrate NaCl concentration as a function of elapsed time. It is readily observed that the ionic solute rejection capability increases with membrane compaction. In addition, the times required to achieve steady-state solute rejection and flux levels are comparable.

### 5.3.3 Membrane Transmission Factors

#### 5.3.3.1 Pressure Dependence

Elimination of the osmotic pressure term in Equation 5.3.3.1A through the use of a distilled water ultrafiltrand permits evaluation of the membrane transmission factor, K, viz.,

$$5.3.3.1A \quad \phi = K(P - \pi')$$

$$\pi' = \alpha \pi; \alpha \geq 1$$

$$\pi = 0$$

$$\therefore \pi' = 0$$

$$5.3.3.1B \quad K = \frac{\phi}{P}$$

FIGURE IX Ultrafiltrate Flux as a Function of Time

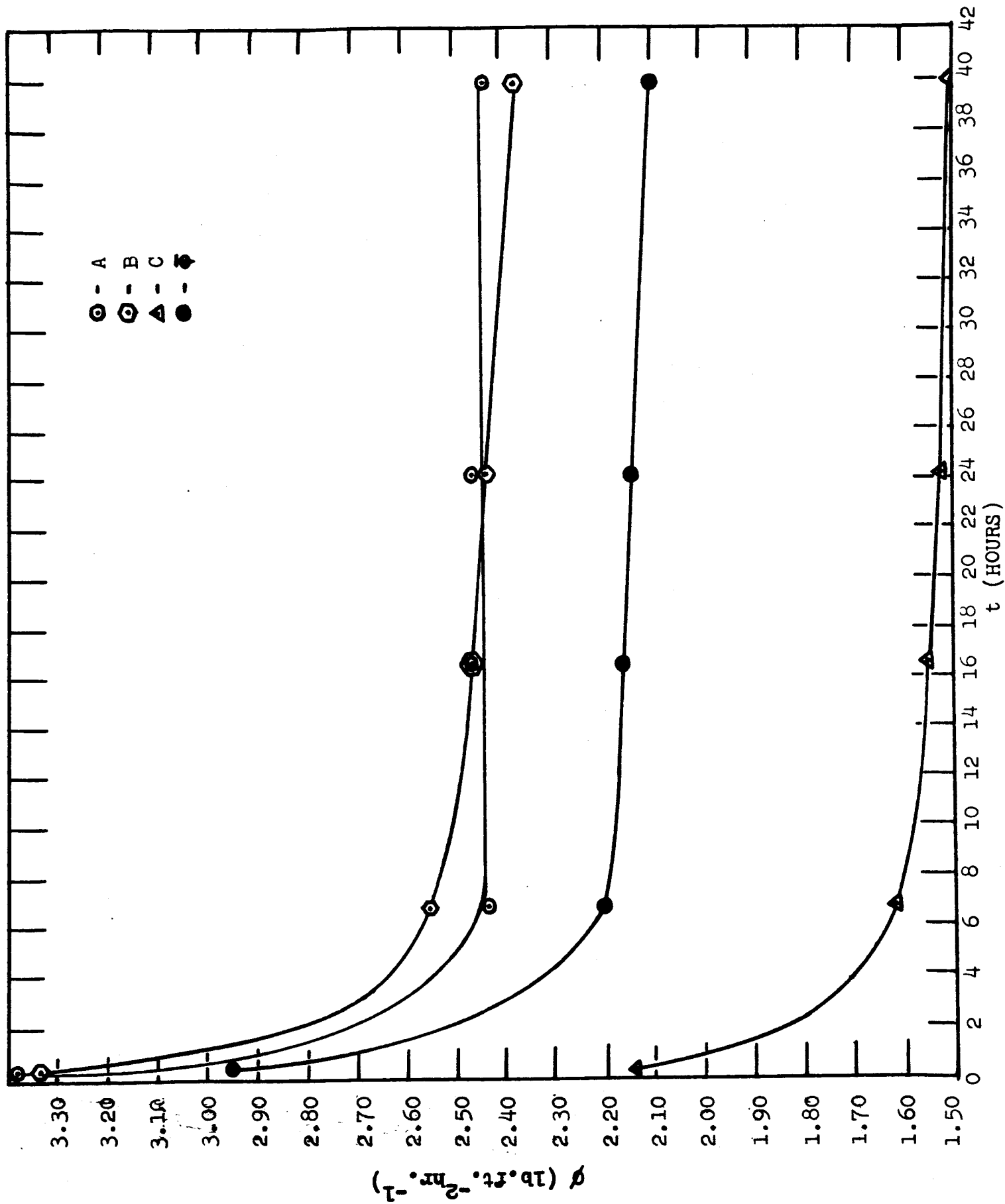
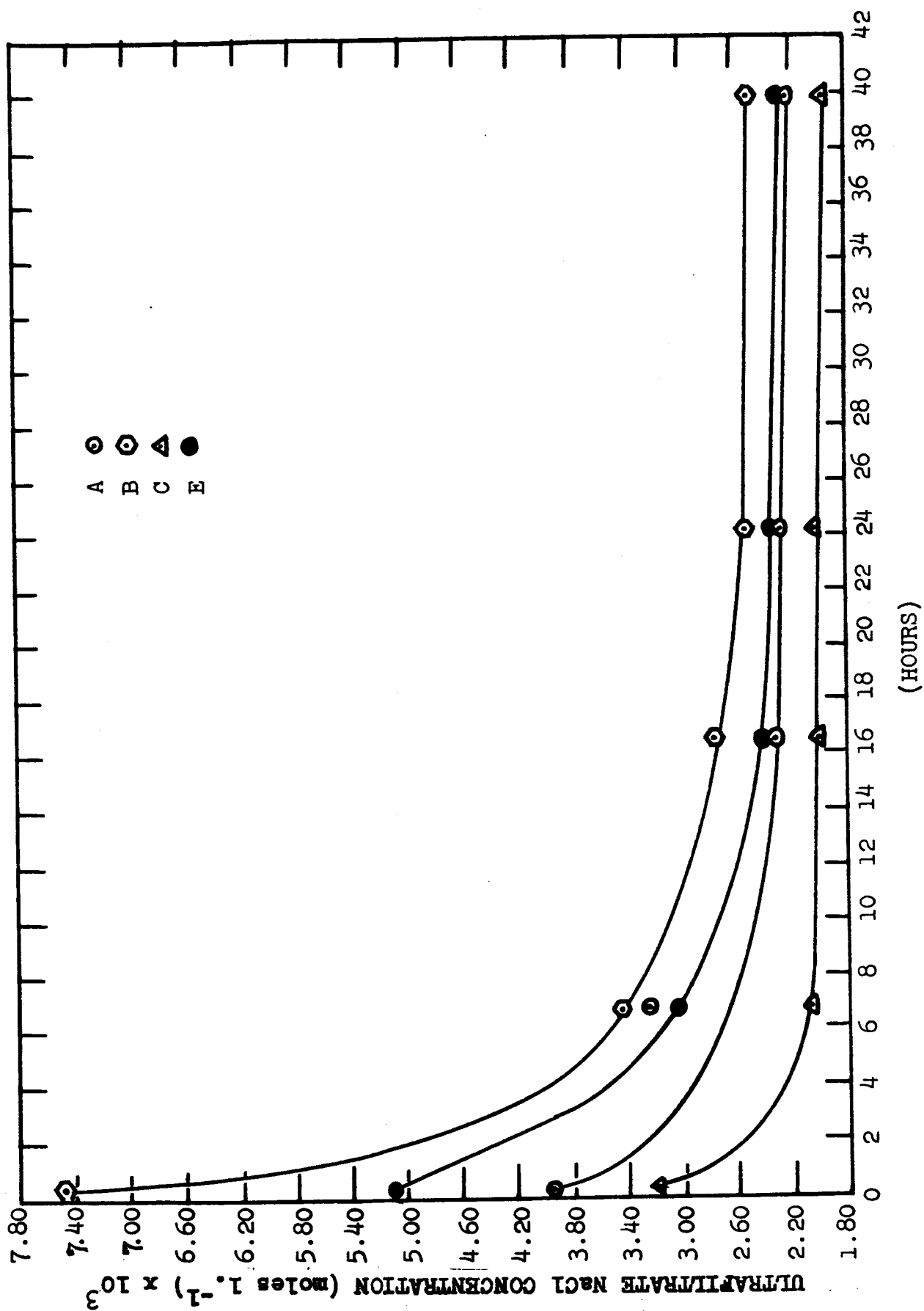


FIGURE X Ultrafiltrate Salt Concentration as a Function of Time



Equation 5.3.3.1B provides a means for evaluating the effect of operating pressure on the membrane transmission factor under isothermal conditions.

The results of such a study are presented in Table 27 and Figures IX and X.

Table 27

Effect of Operating Pressure on Membrane Transmission Factor

Membrane	P(atm.)	$\phi$ (lb.ft. <sup>-2</sup> hr. <sup>-1</sup> )	K(lb.ft. <sup>-2</sup> hr. <sup>-1</sup> atm. <sup>-1</sup> )	t(hrs.)
A	47	3.22	.0681	25.9
	83	4.37	.0525	72.8
	117	4.98	.0428	23.9
	151	5.22	.0346	25.7
	83	3.57	.0428	18.9 <sup>a</sup>
	83	3.09	--	2.4 <sup>b</sup>
B	46	2.05	.0448	25.9
	81	2.87	.0353	72.8
	113	3.40	.0300	23.9
	147	3.68	.0249	25.7
	80	2.47	.0309	18.9 <sup>a</sup>
	80	2.20	--	2.4 <sup>b</sup>

a

Operating pressure reduced from maximum to intermediate value.

b

Ultrafiltrand converted from distilled water to 0.1602 M NaCl solution.

Figure XI constitutes a plot of flux (lb.ft.<sup>-2</sup>hr.<sup>-1</sup>) versus operating pressure (atm.). The observed increase in flux with increasing pressure is consistent with expectations. The non-linearity of the increase reflects the increase in resistance to water transmission with increasing membrane compaction, i.e., increased operating pressure.

The plot of membrane transmission factor (lb.ft.<sup>-2</sup>hr.<sup>-1</sup>atm.<sup>-1</sup>) versus operating pressure (atm.) contained in Figure XII demonstrates the diminishing flux return experienced with the use of increased operating pressure as a result of increased membrane compaction. This negative aspect is overshadowed by the superior solute rejection capability manifested by more compacted membranes.

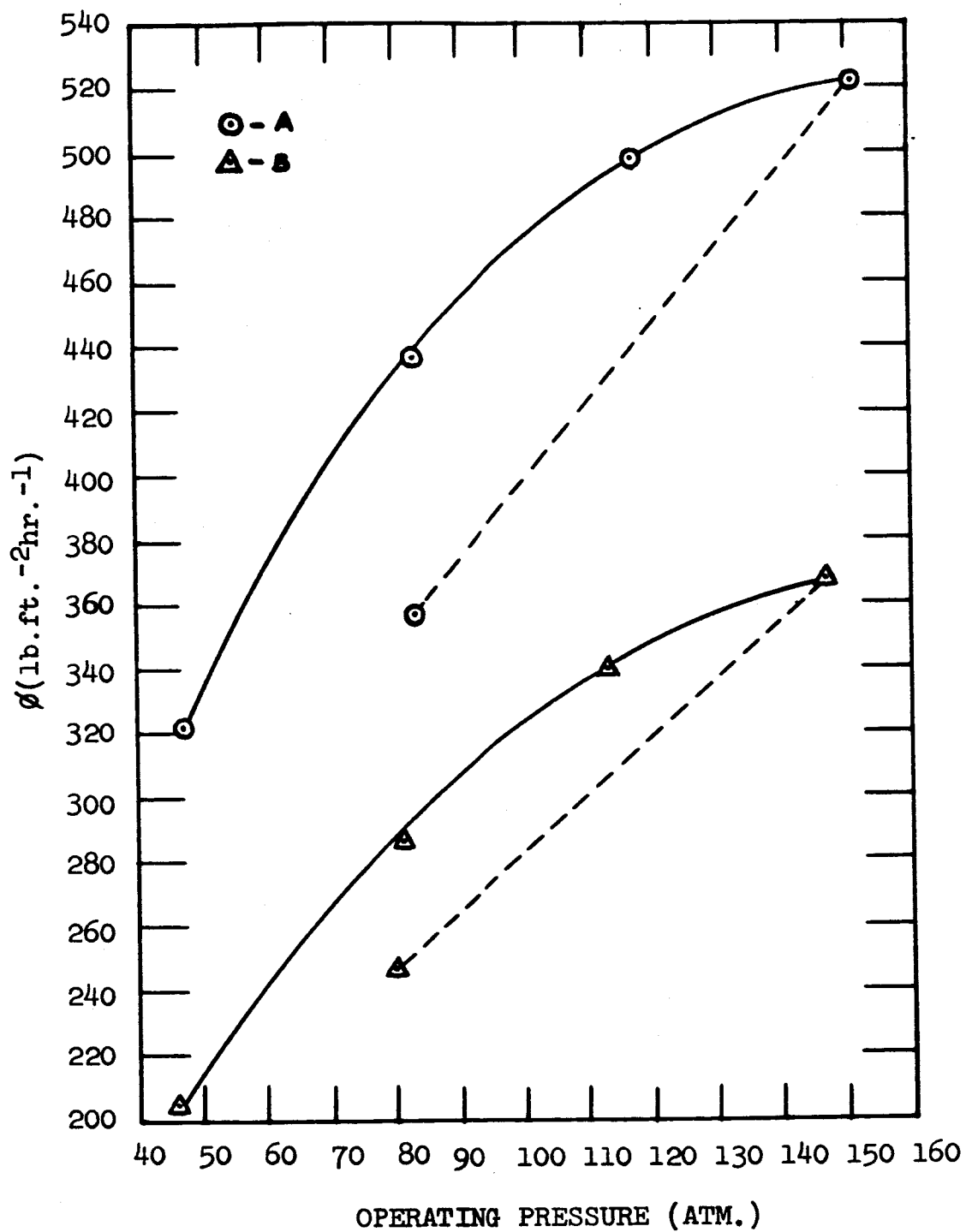
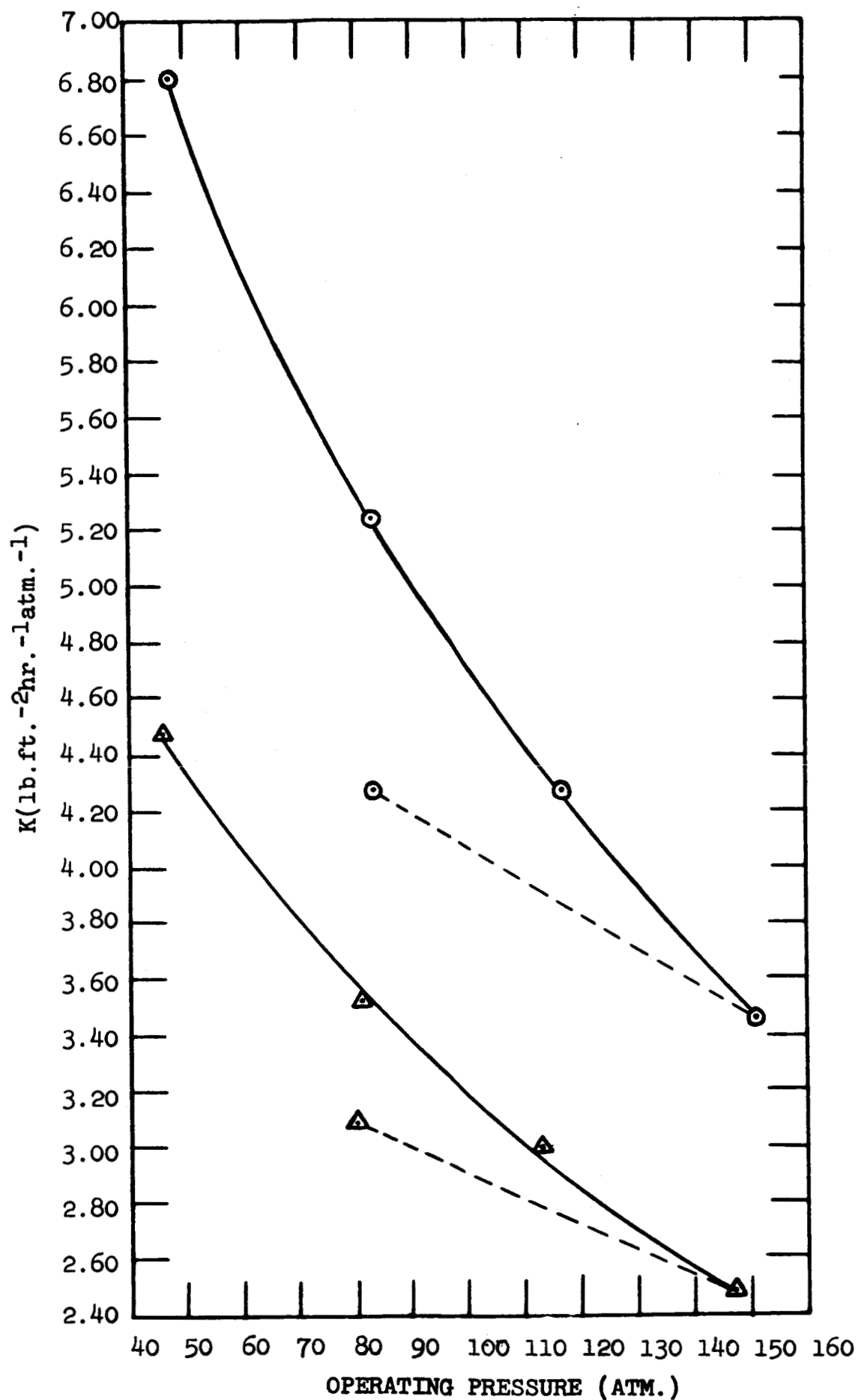


FIGURE XI Ultrafiltrate Flux as a Function of Operating Pressure

FIGURE XII Membrane Constant as a Function of Operating Pressure



In addition, the increased process driving force, i.e., the pressure difference ( $P - \pi'$ ) afforded by greater operating pressures reduces the total theoretical and practical yields.

A semi-logarithmic plot (Fig. XIII) of operating pressure versus membrane transmission factor results in a linear relationship having the general equation

$$5.3.3.1C \quad K = \frac{a - \ln P}{b}$$

where representative values of the characteristic constants are

a	b
5.55	34.95
5.30	58.99

The variation between the two sets of values reflect the observed variation in membrane behavior.

#### 5.3.3.2 Interfacial Osmotic Pressure

The osmotic pressure term,  $\pi'$ , contained in 5.3.3.2A, viz.

$$5.3.3.2A \quad \phi = K(P - \pi')$$

represents the osmotic pressure at the ultrafiltrand membrane interface as contrasted with the bulk ultrafiltrand osmotic pressure,  $\pi$ .

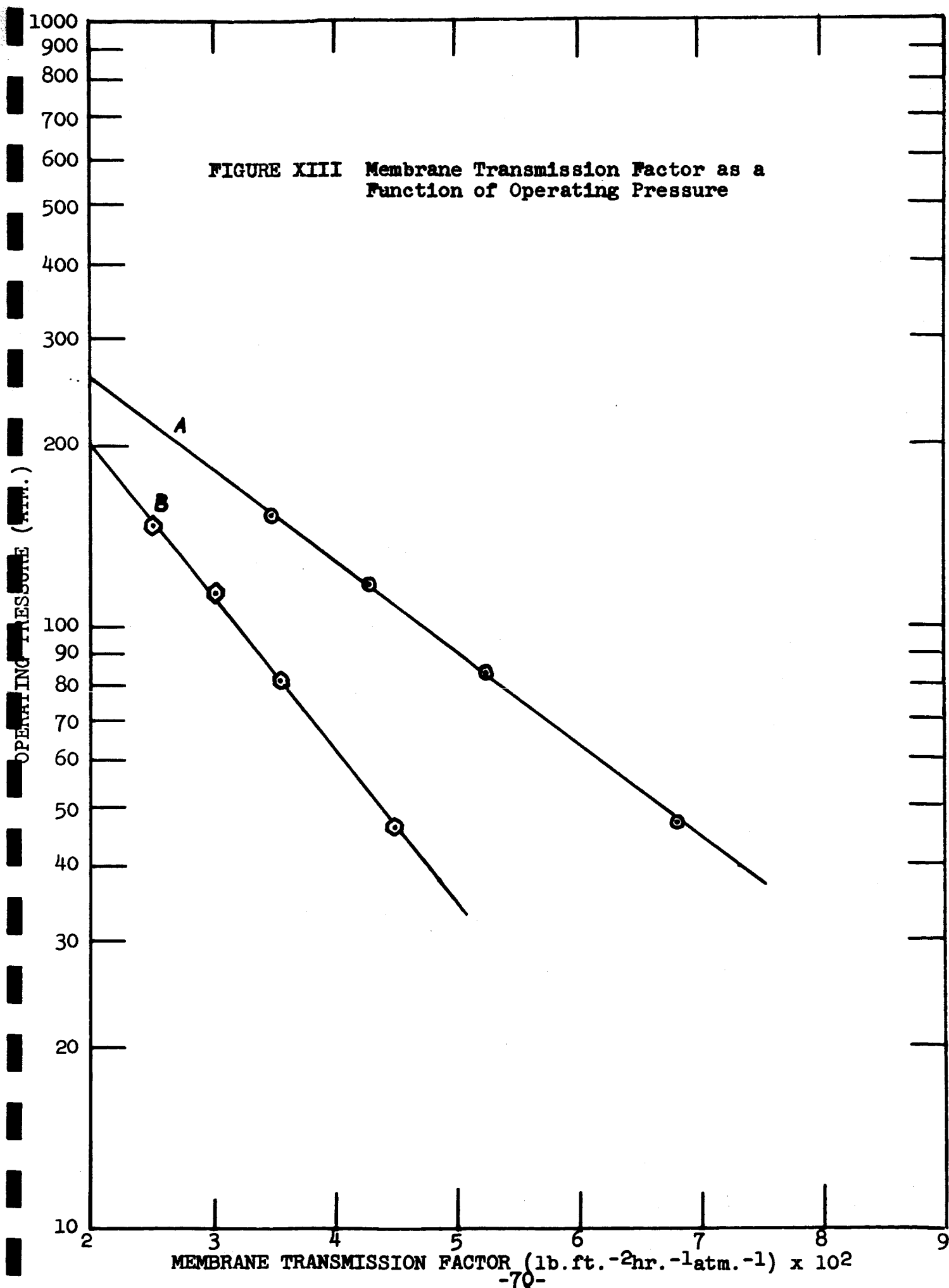
In general, it may be stated that

$$5.3.3.2B \quad \pi' = \alpha \pi ; \alpha \geq 1$$

#### 5.3.3.3 Superficial Velocity Dependence

The ratio of interfacial, i.e., boundary-layer, to bulk osmotic pressure,  $\pi'/\pi$ , is influenced by the superficial velocity,  $v$ , with which the ultrafiltrand passes over the membrane since the latter constitutes the sole means available for dispelling the solute-rich boundary layer.

FIGURE XIII Membrane Transmission Factor as a Function of Operating Pressure



The physical arrangement of the flow cavity relative to the semipermeable membrane as employed during the investigation of the  $v$  dependence of  $\pi' / \pi$  is depicted in Figure XIVA.

It is clear from this Figure that the area perpendicular to the direction of flow is a function of its location on the line connecting the inlet and outlet ports. Since the cylinder height,  $h$ , is constant, a description of the flow area variation reduces to a two-dimensional problem, i.e., -describing the length of chord,  $C$ , as a function of its location- on the line connecting the inlet and outlet ports (see Figure XIVB).

From the general equation of a circle it is readily seen that

$$y = \pm(r^2 - x^2)^{\frac{1}{2}}$$

Inspection of Figure XIVB indicates

$$|y| = \frac{C}{2}$$

or

$$C = 2(r^2 - x^2)^{\frac{1}{2}}$$

Therefore

$$\begin{aligned} A &= hC \\ &= 2h(r^2 - x^2)^{\frac{1}{2}} \end{aligned}$$

The flow area averaged over the diameter,  $\bar{A}$ , may be defined as

$$\bar{A} = \frac{\int A dx}{\int dx}$$

More specifically,

$$\bar{A} = \frac{2h \int_0^2 (r^2 - x^2)^{\frac{1}{2}} dx}{\int_0^2 dx}$$

$$\bar{A} = \frac{h \left[ x(r^2 - x^2)^{\frac{1}{2}} + r^2 \sin^{-1}(x/r) \right]_0^2}{\left[ x \right]_0^2}$$

For:

$$h = 0.0625 \text{ in.}$$

$$r = 2.0000 \text{ in.}$$

$$\bar{A} = 0.1964 \text{ in.}^2$$

Imposing a correction for the fact that the ultrafiltrand enters the flow cavity at a finite velocity, i.e., through a circular port 0.130 in. in diameter

$$\bar{A} = 0.194 \text{ in.}^2 = 1.35 \times 10^{-3} \text{ ft.}^2$$

All reported values of superficial velocity,  $\bar{v}$ , (ft.hr.<sup>-1</sup>) constitute averages calculated by dividing the ultrafiltrand volumetric flow rate (ft.<sup>3</sup>hr.<sup>-1</sup>) by the average flow area (1.35 x 10<sup>-3</sup> ft.<sup>2</sup>).

Figure XV presents a plot of flux (lb.ft.<sup>-2</sup>hr.<sup>-1</sup>) versus operating time (hours) for the following consecutive conditions:

a. Membrane compaction using distilled water ultrafiltrand ( $\pi = 0$ ;  $\bar{v} = 1095 \text{ ft.hr.}^{-1}$ );

b. 0.2082 M NaCl solution ( $\pi = 11.0 \text{ atm.}$ ;  $\bar{v} = 1095 \text{ ft.hr.}^{-1}$ );

c. Average ultrafiltrand superficial velocity ( $\bar{v} = 811 \text{ ft.hr.}^{-1}$ );

d. Average ultrafiltrand superficial velocity

$$(\bar{v} = 312 \text{ ft.hr.}^{-1});$$

e. Average ultrafiltrand superficial velocity

$$(\bar{v} = 57 \text{ ft.hr.}^{-1});$$

f. Average ultrafiltrand superficial velocity

$$(\bar{v} = 982 \text{ ft.hr.}^{-1});$$

g. Reconversion of ultrafiltrand to distilled water

$$(\bar{\pi} = 0; \bar{v} = 8.16 \text{ cm.sec.}^{-1}).$$

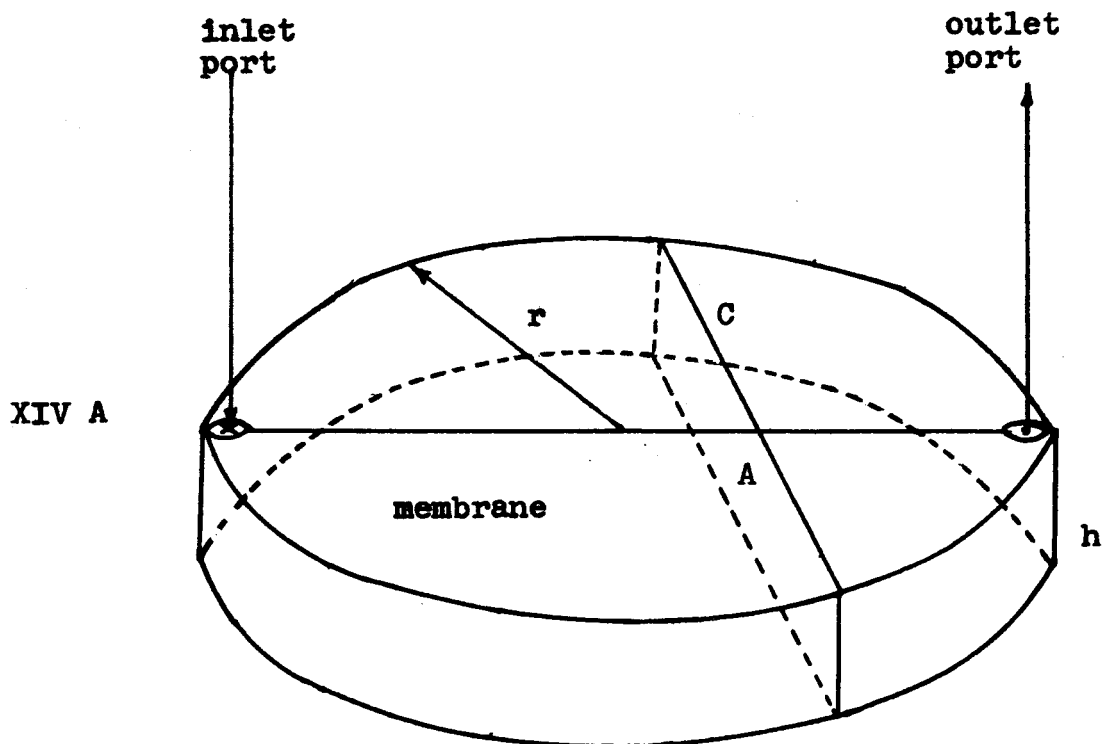
The above information and results derived are summarized in Table 28.

It is particularly noteworthy that the flux value obtained at the termination of the experiment (g) with a distilled water ultrafiltrand ( $\bar{\pi}_R = 0$ ) is 97.2 percent of the value at the inception of the experiment. This suggests that membrane compaction and membrane deterioration effects have been eliminated from the experiment.

Figure XVI constitutes a plot of flux ( $\text{lb.ft.}^{-2}\text{hr.}^{-1}$ ) versus average ultrafiltrand superficial velocity ( $\text{ft.hr.}^{-1}$ ). Arrowheads are used to indicate the direction in which the independent variable, viz.  $\bar{v}$ , was changed. It is apparent from the solid-line graph that product water flux decreases smoothly with diminishing ultrafiltrand superficial velocity. The dotted line indicates the result of causing  $\bar{v}$  to resume a value closely approaching the maximum.

The failure of the flux to return along the previously determined curve suggests the existence of an hysteresis effect. It should be noted that, in keeping with expectations, no dependence of flux upon superficial velocity is observed using a non-solute bearing ultrafiltrand, viz. distilled water.

FIGURE XIV Geometric Analog of Cell Flow Cavity



$r$ : cylinder radius = 2.00 in.  
 $h$ : cylinder height = .0625 in.  
 $A$ : flow area  
 $C$ : chord

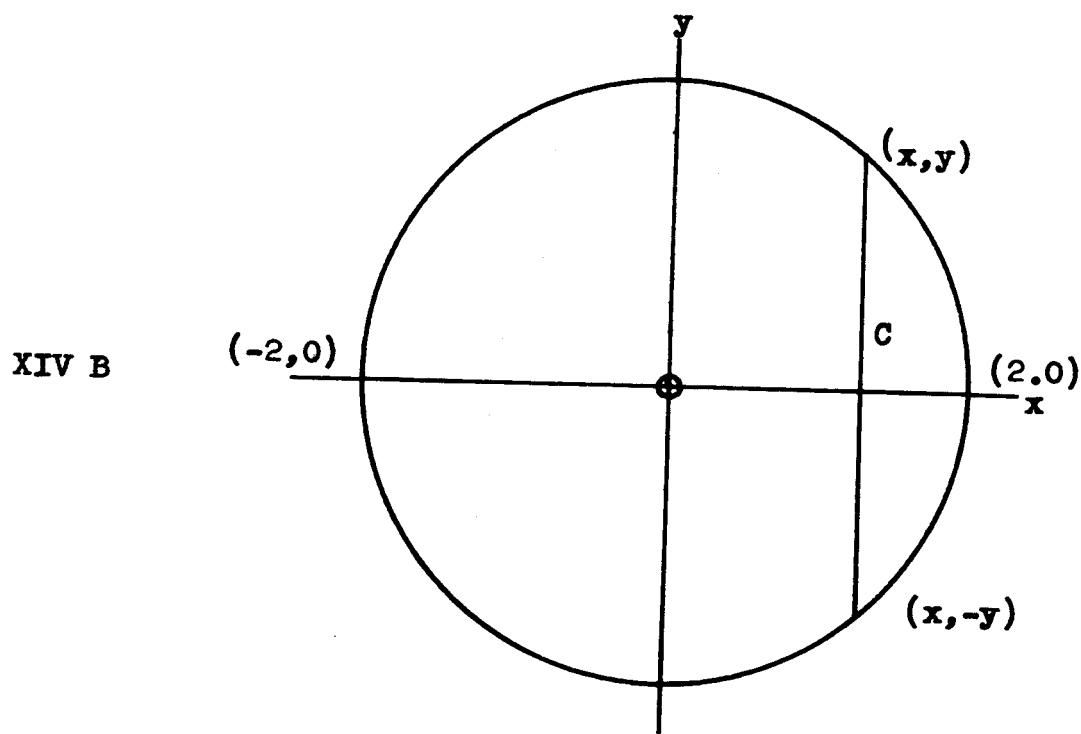


FIGURE XV Ultrafiltrate Flux as a Function of Time

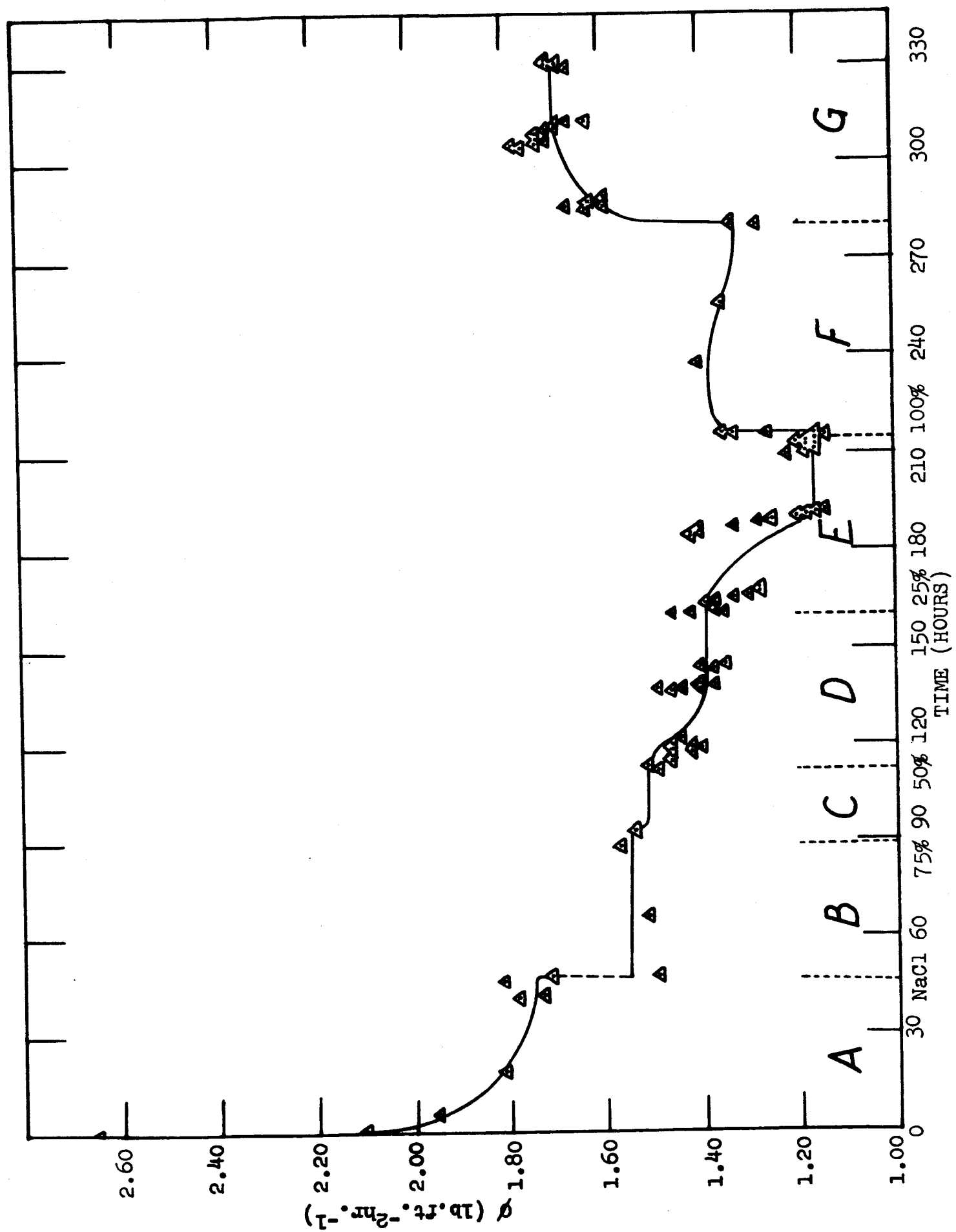
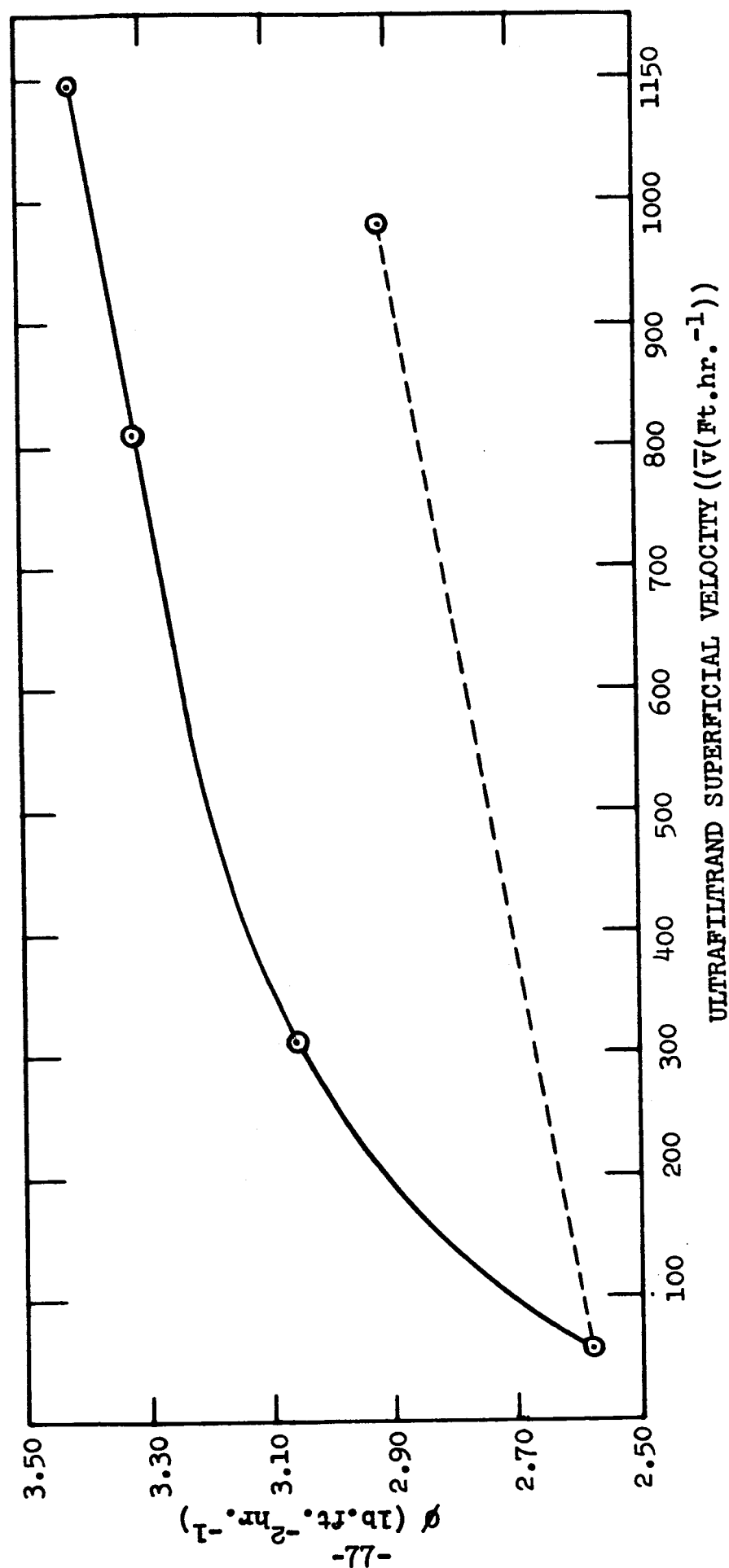


Table 28  
Effect of Superficial Velocity on Flux

Seg- ment	Ultra- filtrand	$\bar{v}$ (ft.hr. <sup>-1</sup> )	$\phi$ (lb.ft. <sup>-2</sup> ) hr.	K (lb.ft. <sup>-2</sup> ) hr.atm.	$[Cl^-]_R$ (ppm)	$\pi_R$ (atm.)	$\pi'_R$ (atm.)	$\pi'_R$ (ppm)	$\pi_R$ (ppm)	hrs.
A	distilled water	1095	3.86	.0262	0	0	0	0	0	48.0
B	NaCl solution	1095	3.42	-	7382	11.0	17.0	1.55	102	19.3
C	NaCl solution	811	3.32	-	7411	11.1	20.0	1.80	119	45.8
D	NaCl solution	312	3.06	-	7879	11.7	30.4	2.60	102	47.6
E	NaCl solution	57	2.58	-	8520	12.7	40.9	3.22	130	54.8
F	NaCl solution	982	2.91	-	8024	12.0	36.4	3.03	163	67.5
G	distilled water	964	3.75	.0254	0	0	0	-	0	49.5

Notes: Operating pressure: 147 atm.  
Operating Temperature: 25°C.  
Ultrafiltrand flow area: 1.35 x 10<sup>-3</sup> ft.<sup>2</sup>

FIGURE XVI Ultrafiltrate Flux as a Function of Ultrafiltrand Velocity



The boundary-layer osmotic pressure,  $\pi'$ , is calculable from Equation 5.3.1A, while the bulk osmotic pressure,  $\pi$ , at low solute concentrations may be determined from freezing point depression measurements. A semi-logarithmic plot of the ratio  $\pi'/\pi$  versus average ultrafiltrand superficial velocity results in a linear relationship (see Figure XVII) having the equation

$$5.3.3.3A \quad \frac{\pi'}{\pi} = e^{-7.61 \times 10^{-4} \bar{v}} + 1.20$$

where  $\bar{v}$  is expressed in ft.hr.<sup>-1</sup>

Solving equation 5.3.3.3A for the case in which  $\bar{v}=0$

$$\frac{\pi'}{\pi} = 3.32$$

For the case when  $\pi' = \pi$

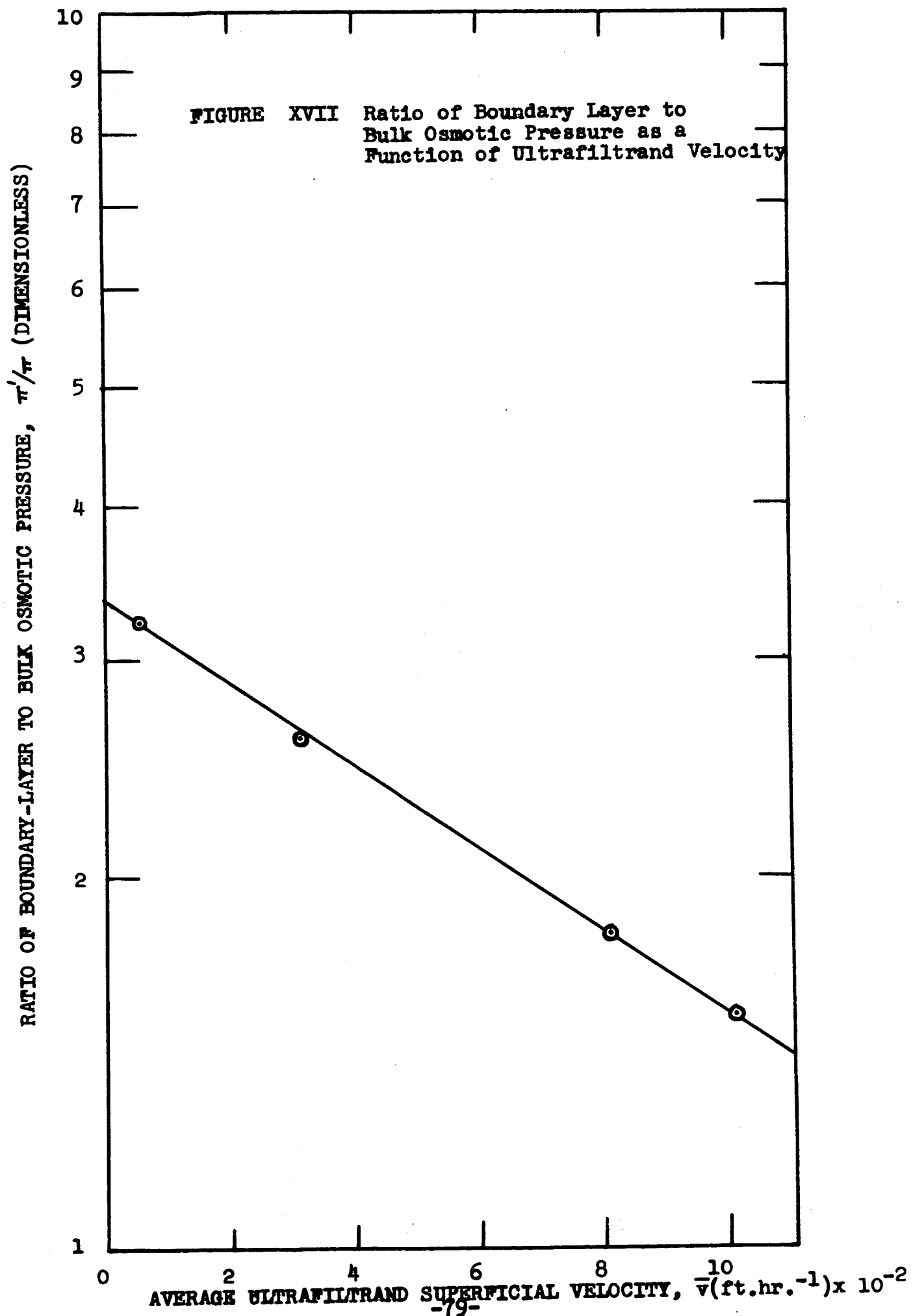
$$\bar{v}_c = 1580 \text{ ft.hr.}^{-1}$$

This constitutes an experimentally unverified but potentially important design consideration. The experimental apparatus employed in this study permitted a maximum superficial velocity of approximately 1100 ft.hr.<sup>-1</sup>

#### 5.3.4 Concentration Dependence

The effect of ultrafiltrand solute concentration on the boundary layer-to-bulk osmotic pressure ratio,  $\pi'/\pi$  at constant superficial velocity, viz. 855 ft.hr.<sup>-1</sup> was studied.

The procedure followed involved membrane compaction using a distilled water ultrafiltrand in order to evaluate the membrane transmission factor, K. Subsequently, the ultrafiltrand was converted to 0.2M NaCl and the resultant flux recorded when sufficient time had elapsed to permit the establishment of the new equilibrium conditions. In a similar manner, the ultrafiltrand NaCl concentration was changed by  $\sim 0.5$  molar increments until a final concentration of 2.8 M was attained. Finally, the NaCl



solution which constituted the ultrafiltrand was replaced with distilled water to permit redetermination of the membrane transmission factor, allowing ample time for elution of NaCl contained in the membrane.

The initial and final K values for the 160 hour run were .0144 and .0083 lb.ft.<sup>-2</sup>hr.<sup>-1</sup>atm.<sup>-1</sup>, respectively.

Inasmuch as the boundary-layer osmotic pressure is K dependent, the assumption that K decreased linearly during the elapsed time span was made. Interpolated values of K were used to calculate the boundary-layer osmotic pressure. Bulk osmotic pressure values were obtained from the literature.<sup>31</sup> The ratio of the two osmotic pressure terms is plotted as a function of ultrafiltrand NaCl concentration in Figure XVIII.

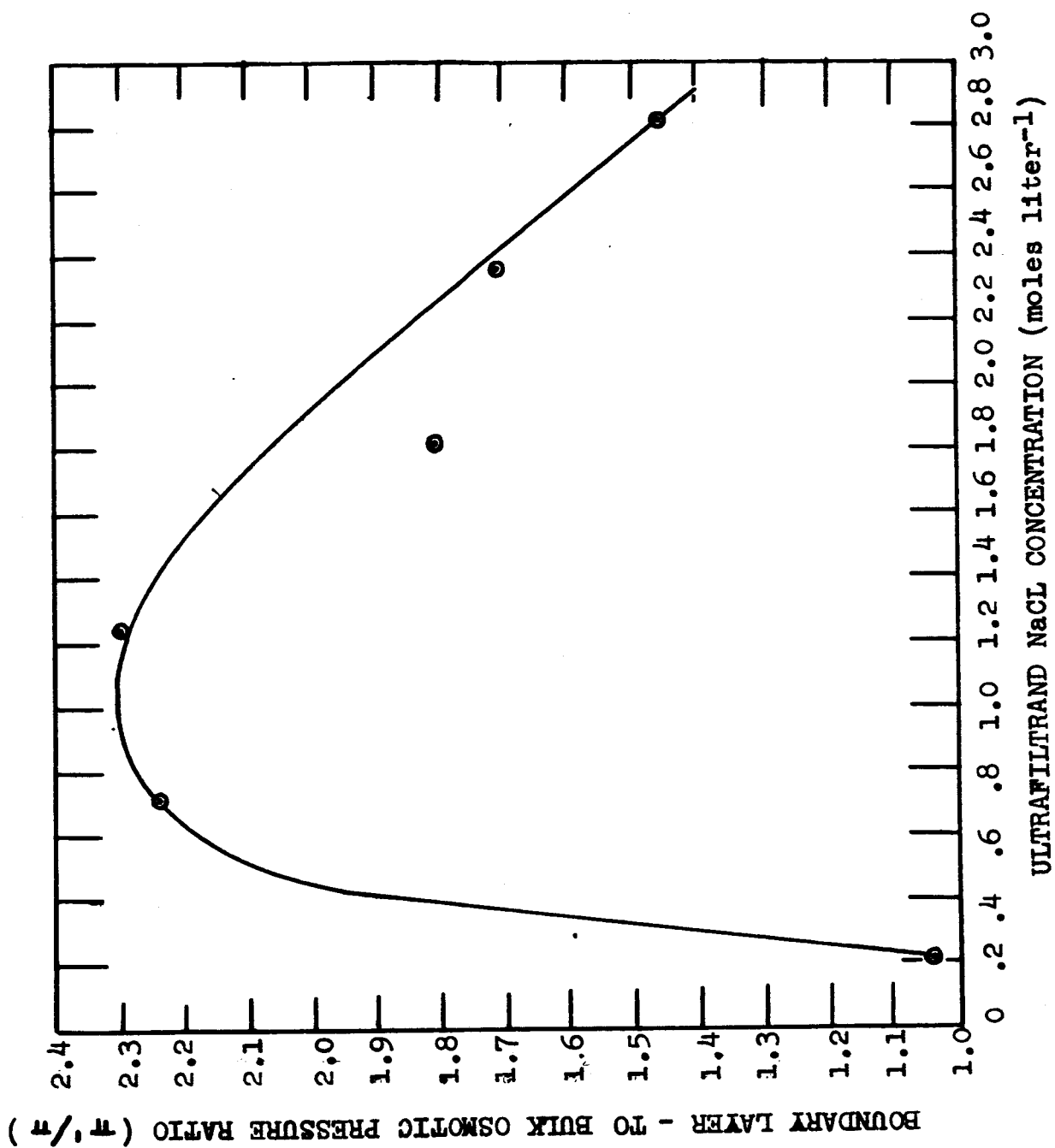
Admittedly, the inconstancy of the membrane transmission due to non-establishment of equilibrium factor renders the results qualitative. Mechanistically, it might be expected that the diminution in flux which occurs with increasing ultrafiltrand solute concentration, i.e., increasing bulk osmotic pressure, would decrease the rate at which rejected solute ions accumulate at the ultrafiltrand-membrane interface. As a consequence, the ratio of boundary layer-to-bulk osmotic pressure would decrease with increasing ultrafiltrand solute concentration.

A corollary of this would be an expected dependence of  $\Pi'$  on the membrane transmission factor at any given ultrafiltrand solute, concentration. Specifically,  $\Pi'$  and therefore  $\Pi'/\Pi$  would be expected to vary directly with K.

#### 5.3.4.1 Effect of Ultrafiltrand Solute Concentration on Solute Rejection and Flux

The experiments reported in this section were all conducted under conditions of non-steady-state ultrafiltrand solute

FIGURE XVIII Ratio of Boundary Layer to Bulk Osmotic Pressure as a Function of Ultrafiltrand Salt Concentration



concentration in order to secure information regarding the dynamics of the ultrafiltration operation. Procedurally, this involved continuous ultrafiltrate collection.

In the initial study an idealized ultrafiltrand, i.e., 0.2 M NaCl, (having an osmotic pressure comparable to that of electrolyzed urine) was employed in order to avoid the compositional indeterminacy characteristic of pre-treated urine. Flux values, and ultrafiltrate and ultrafiltrand chloride concentrations were recorded as a function of operating time until greater than 90% of the volume of the initial charge was recovered. At this time, the ultrafiltrate and residual ultrafiltrand were recombined to be ultrafiltered again. This procedure was repeated twice to provide an indication of membrane longevity.

Table 29 contains data pertinent to this experiment.

Table 29

Cyclic Ultrafiltration of Re-constituted NaCl

Time (hrs.)	Flux (lb.ft. <sup>-2</sup> hr. <sup>-1</sup> )	NaCl Concentration (moles/liter)	
		Ultrafiltrand	Ultrafiltrate
0.0	2.45	.1995	-
2.3	2.36	.2073	.00214
25.8	2.16	.3126	.00324
38.3	1.98	.4208	.00465
54.0	1.72	.6531	.00911
60.2	1.57	.8747	.01303
69.1	1.23	1.2982	.02671
81.2	0.40	2.1144	.10202
-----			
82.3	2.16	.2609	.00412
93.7	2.09	.2801	.00324
100.4	2.05	.2790	.00367
124.4	1.92	.4781	.00508
142.2	1.76	.7482	.00965
156.5	1.19	1.3193	.02736
169.3	0.40	2.1387	.09001
-----			
170.4	2.03	.1956	.01021
196.0	2.03	.2951	.00341
229.4	1.94	.6189	.00826
239.6	1.58	.8918	.01371
260.6	0.46	2.0604	.08349

Figure XIX is a plot of ultrafiltrate versus ultrafiltrand concentration for the subject experiment. It is immediately observable that data obtained from each of the three consecutive separations lie on essentially the same curve. This attests to the constancy of performance exhibited by the membrane during its 260-hour operating period.

A linear relationship is observed upon plotting reciprocal ultrafiltrate concentration versus reciprocal ultrafiltrand concentration as shown in Figure XX (points  $\alpha$  and  $\beta$  may be excluded from consideration on experimental grounds). The equation of said line may be represented as

$$5.3.4.1A \quad M_e = \frac{M_R}{1.022 \times 10^2 - 37.58 M_R}$$

A plot of flux in  $\text{lb.ft.}^{-2}\text{hr.}^{-1}$  as a function ultrafiltrand concentration in  $\text{gram-moles liter}^{-1}$  as shown in Figure XXI possesses a distinct linear character. It may be described by the equation

$$5.3.4.1B \quad \phi = -0.954 M_R + 2.44$$

It is of interest to compare the above relationship with equation 5.3.1A rewritten as

$$5.3.4.1C \quad \phi = -K \Pi' + KP$$

Values of the membrane transmission factor,  $K$ , and the operating pressure,  $P$ , for the experiment under discussion provide an empirical y-intercept of  $2.48 \text{ lb.ft.}^{-2}\text{hr.}^{-1}$  as compared with the predicted value of  $2.44 \text{ lb.ft.}^{-2}\text{hr.}^{-1}$  from equation 5.3.4.1B. This degree of correlation is well within experimental error.

An immediate consequence of this agreement is a suggestion to investigate the relationship between the boundary-layer osmotic pressure,  $\Pi'$ , and the molarity of the solute species in the ultrafiltrand,  $M_R$ .

FIGURE XIX ULTRAFILTRATE CONCENTRATION AS A FUNCTION OF ULTRAFILTRAND CONCENTRATION

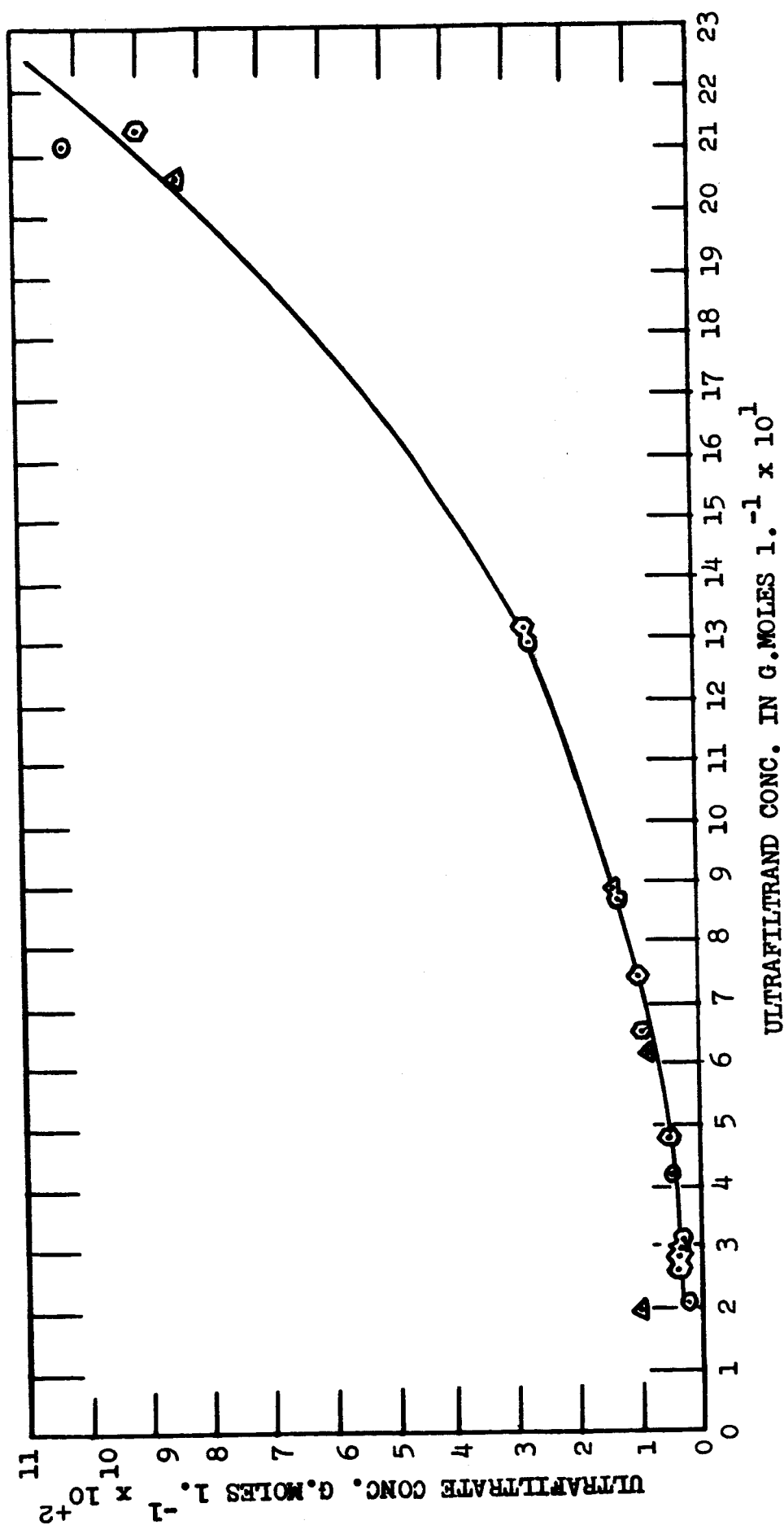


FIGURE XX Ultrafiltrate Chloride Concentration as a Function of Ultrafiltrand Chloride Concentration

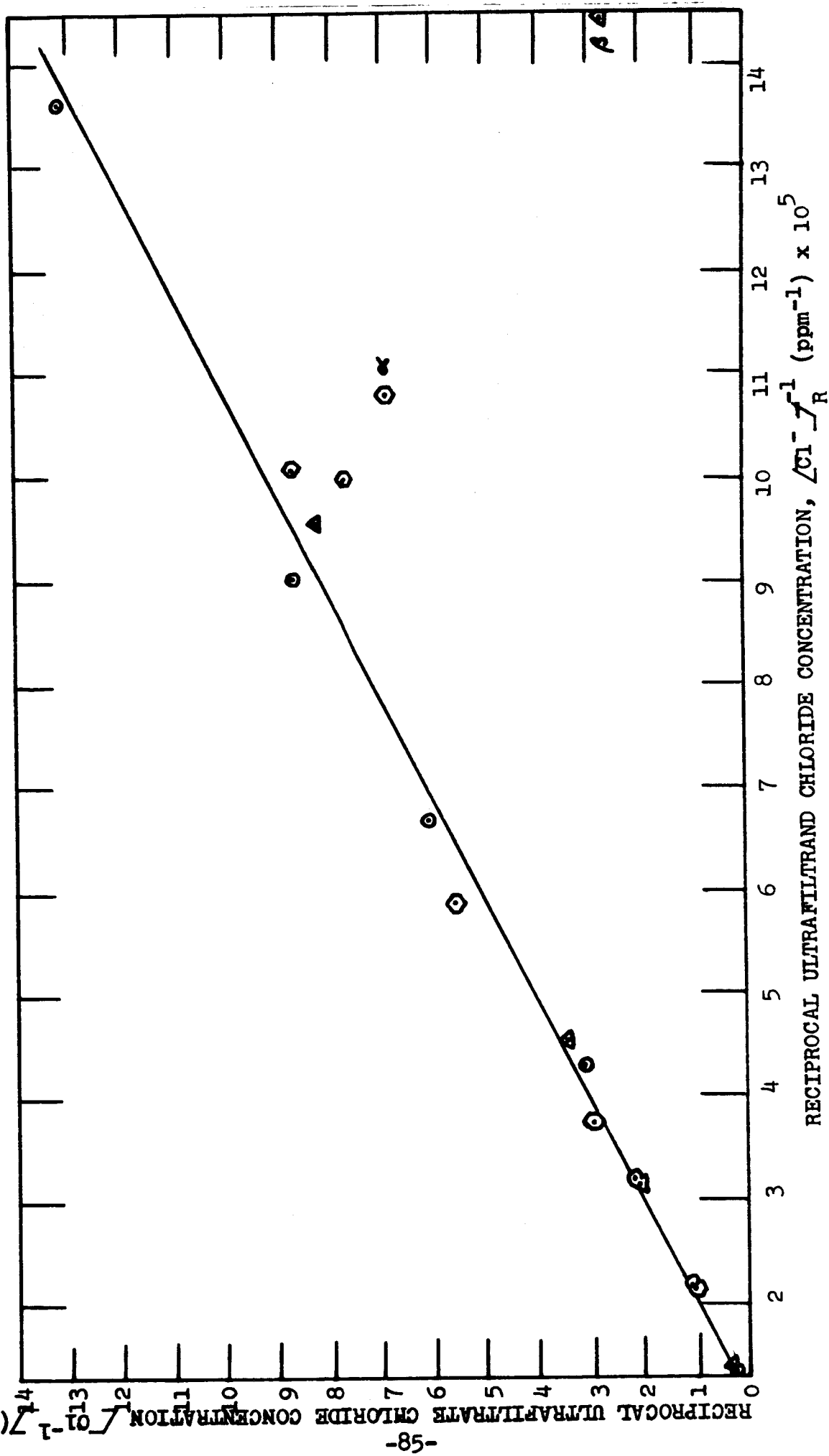
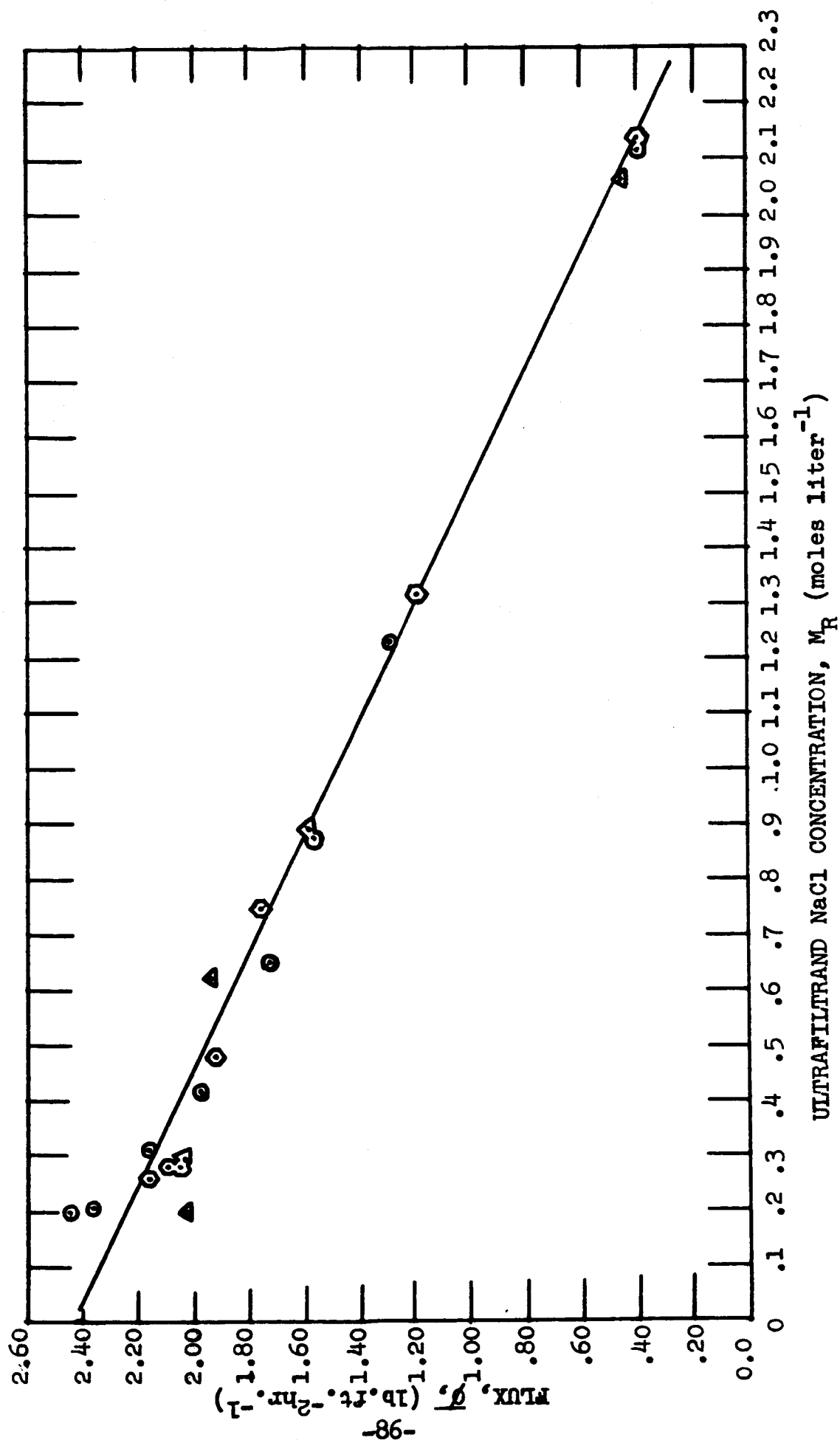


FIGURE XXI Ultrafiltrate Flux as a Function of Ultrafiltrand Salt Concentration



It has been previously shown (at a single value of  $M_R$ ) that

$$5.3.4.1D \quad \bar{\pi} = \pi e^{f(\bar{v})}$$

where  $\bar{\pi}$  represents the bulk ultrafiltrand osmotic pressure and  $f(\bar{v})$  is defined as some function of the average ultrafiltrand superficial velocity.

Furthermore, a practical osmotic coefficient,  $g$ , may be defined such that

$$5.3.4.1E \quad g \equiv \frac{\bar{\pi}_{\text{real}}}{\pi_{\text{ideal}}}$$

Since

$$5.3.4.1F \quad \pi_{\text{ideal}} = MRT$$

where

M: Solute molarity  
R: universal gas constant  
T: absolute temperature

or

$$5.3.4.1G \quad \bar{\pi}_{\text{real}} = gMRT$$

However, it is also true that

$$g = s(M)$$

Data pertinent to aqueous sodium chloride solutions presented by Robinson and Stokes<sup>31</sup> are excellently fitted by the equation

$$5.3.4.1H \quad g = .921 + 1.095 \times 10^{-3} M^{-1} + 1.55 \times 10^{-2} M^2$$

Substituting the above in equation 5.3.4.1I one obtains

$$5.3.4.1I \quad \bar{\pi}_{\text{real}} = RT(1.55 \times 10^{-2} M^3 + .921M + 1.095 \times 10^{-3})$$

Since  $0 < M_e < 2.5$  gm.-moles liter<sup>-1</sup>, the maximum contribution of the first term of the polynomial (i.e., at  $M_R = 2.5$  gm.-moles liter<sup>-1</sup>) is only 10.5 percent.

Simplifying equation 5.3.4.1I further one may write

$$5.3.4.1J \quad \pi_R = RT(.921 M_R + 1.55 \times 10^{-2} M_R^3)$$

and, subsequently,

$$5.3.4.1K \quad \pi' = RTe^{f(\nabla)} (.921 M_R + 1.55 \times 10^{-2} M_R^3)$$

Finally,

$$5.3.4.1L \quad \phi = KRTe^{f(\nabla)} (.921 M_R + 1.55 \times 10^{-2} M_R^3) + KP$$

It is imperative to realize that the solute concentration dependence of  $\pi'$  (see Figure XVIII) has not been incorporated in the above expression.

### 5.3.5 Potable Water Recovery

The following equation describes solute transmission through the ultrafilter.

$$V_R M_R = V_R^o M_R^o - V_E \bar{M}_E$$

where

- V: volume
- M: solute concentration
- R: ultrafiltrand
- E: ultrafiltrate
- o: initial conditions

and  $\bar{M}_E$ , the volume-averaged ultrafiltrate solute concentration is defined as

$$\bar{M}_E = \frac{\int_0^{V_E} M_E dV_E}{\int_0^{V_E} dV_E}$$

Table 30 contains pertinent data from the previously discussed experiment in which the ultrafiltrand employed was an aqueous sodium chloride solution.

Table 30

Ultrafiltration of Aqueous Sodium Chloride Solution

$V_E$ (Liters) <sup>a</sup>	$M_E$ (gm.-moles liter) $\times 10^3$
0.825	2.14
8.605	3.24
12.025	4.65
15.955	9.11
17.235	13.03
18.855	26.71
20.085	102.02

---

<sup>a</sup>  $V_R^0 = 21.7$  liters

A plot of fractional recovery,  $V_E/V_R^0$ , versus reciprocal ultrafiltrate NaCl concentration,  $M_E$ , (liters gram-mole<sup>-1</sup>) (Figure XXII) produces a linear relationship having the equation

$$5.3.5A \quad M_E = \frac{1.85 \times 10^{-3}}{0.940 - (V_E/V_R^0)}$$

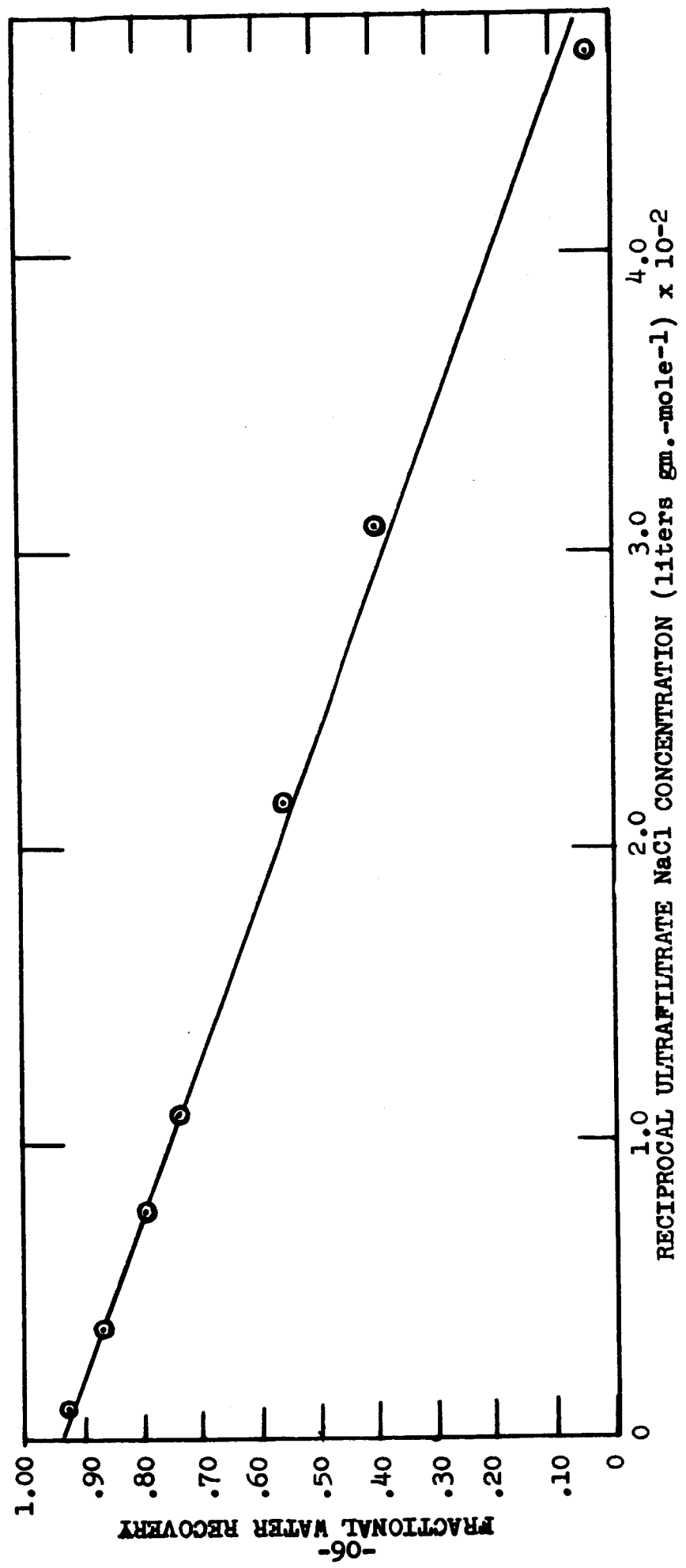
Therefore

$$\begin{aligned} \int_0^{V_E} M_E dV_E &= 1.85 \times 10^{-3} \int_0^{V_E} \frac{dV_E}{.940 - (V_E/V_R^0)} \\ &= -1.85 \times 10^{-3} V_R^0 \ln [.940 - (V_E/V_R^0)] \Big|_0^{V_E} \\ &= -1.85 \times 10^{-3} V_R^0 \ln \left[ 1 - \frac{(V_E/V_R^0)}{.940} \right] \end{aligned}$$

And 5.3.5B

$$\bar{M}_E = -1.85 \times 10^{-3} \frac{V_R^0}{V_E} \ln \left[ 1 - \frac{(V_E/V_R^0)}{.940} \right]$$

FIGURE XXII Fractional Water Recovery as a Function of Ultrafiltrate NaCl Concentration



If the acceptable average chloride concentration is established at  $250 \text{ mg.l}^{-1}$  in accordance with USPHS standards

$$\bar{M}_E = 7.05 \times 10^{-3} \text{ gm-moles liter}^{-1}$$

and equation 5.3.5B becomes

$$\frac{V_E}{V_R^0} = .940 \left[ 1 - e^{-3.81(V_E/V_R^0)} \right]$$

By a trial-and-error solution it is ascertained that

5.3.5C  $\frac{V_E}{V_R^0} \approx 0.92$

It should be emphasized that while the relationships presented above are demonstrably representative of the experimental data, prudence should be employed in extrapolation in view of the mathematical limitations of the algorithms.

### 5.3.6 Ultrafiltration of Electrolyzed Urine

Electrolyzed urine was employed as the ultrafiltrand in an experiment analogous to that conducted with aqueous sodium chloride solution.

Initially, distilled water was employed as the ultrafiltrand for a period of 71.4 hours to insure complete membrane compaction. Subsequently 20.3 l of an electrolyzed urine ultrafiltrand was imposed on the system. When all but the systemic hold-up volume had been ultrafiltered, the electrolyzed urine was reconstituted for a second pass.

Pertinent data collected during this experiment is tabulated in Table 31.

Table 31

Cyclic Ultrafiltration of Reconstituted Electrolyzed Urine

Ultrafiltrand Total Solids (mg.l. <sup>-1</sup> )	Flux (lb.ft. <sup>-2</sup> hr. <sup>-1</sup> )	Ultrafiltrate Total Solids (mg.l. <sup>-1</sup> )
18600	1.34	484
21800	1.30	594
27750	1.22	818
40500	1.18	1272
64300	.89	2653
105650	.65	5943
198200	.32	16837
18800	1.21	777
22950	1.11	1010
38850	.98	1842
52400	1.00	2681
76750	.66	4578
168550	.39	14479

The tabulated data is presented graphically in Figures XXIII, XXIV, and XXV.

The most prominent difference between these results and those obtained using a sodium chloride ultrafiltrand is the slight diminution in membrane performance upon reprocessing the reconstituted ultrafiltrand. Without conducting additional investigations it is impossible to do more than delineate feasible explanations for the observed disparity. Among these must be included.

a. Intrinsically different membrane behavior.

b. Effects peculiar to unidentified non-ionic oxidation products formed during urine electrolysis.

It should be emphasized that upon reconstituting the electrolyzed urine ultrafiltrand, the system was allowed to operate for 50.8 hours with all ultrafiltrate being recycled directly to the ultrafiltrand reservoir in order to allow sufficient time for the membrane to come to equilibrium with the new

FIGURE XXIII Ultrafiltrate Flux as a Function of Ultrafiltrand Solids Concentration

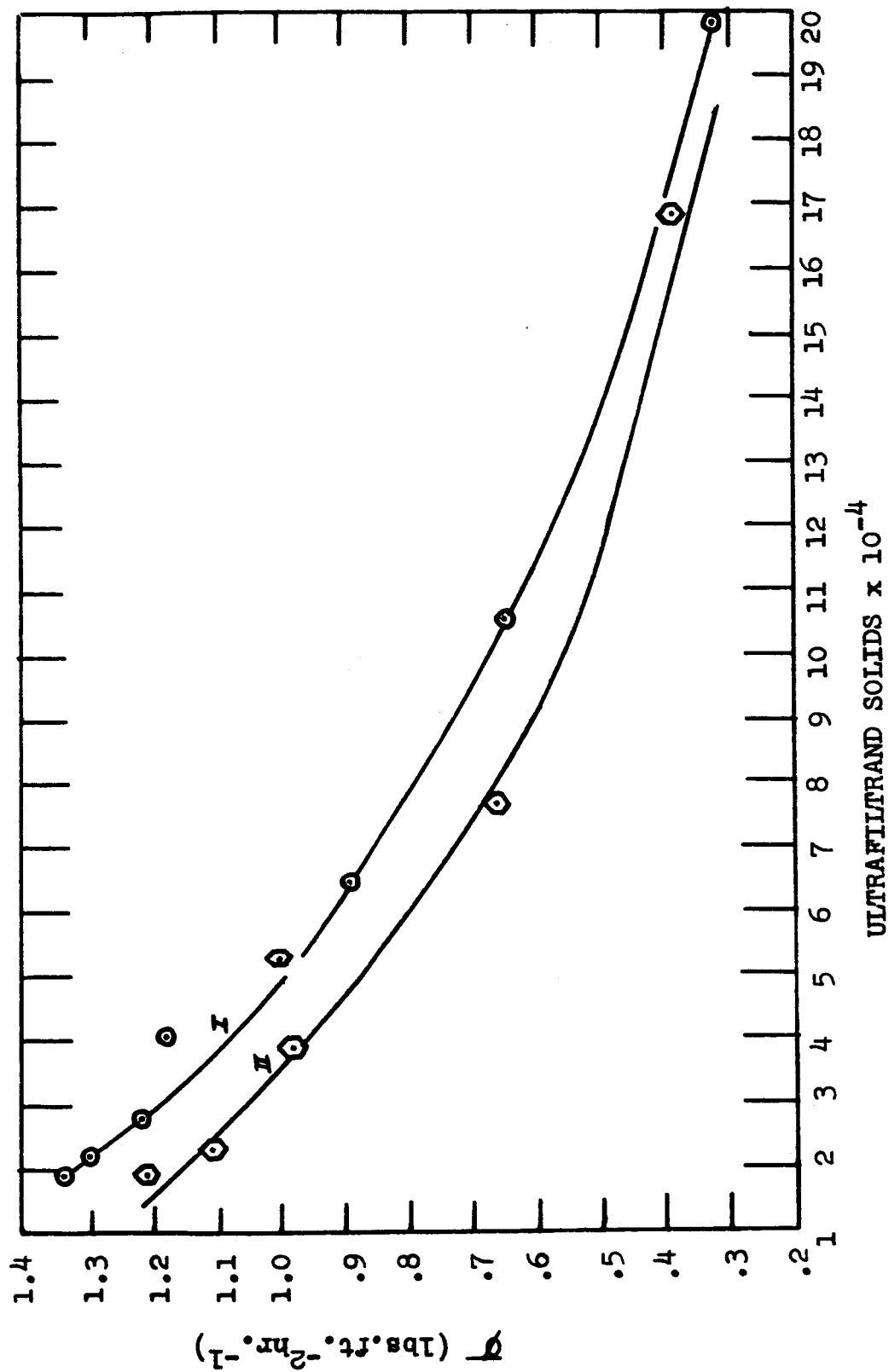
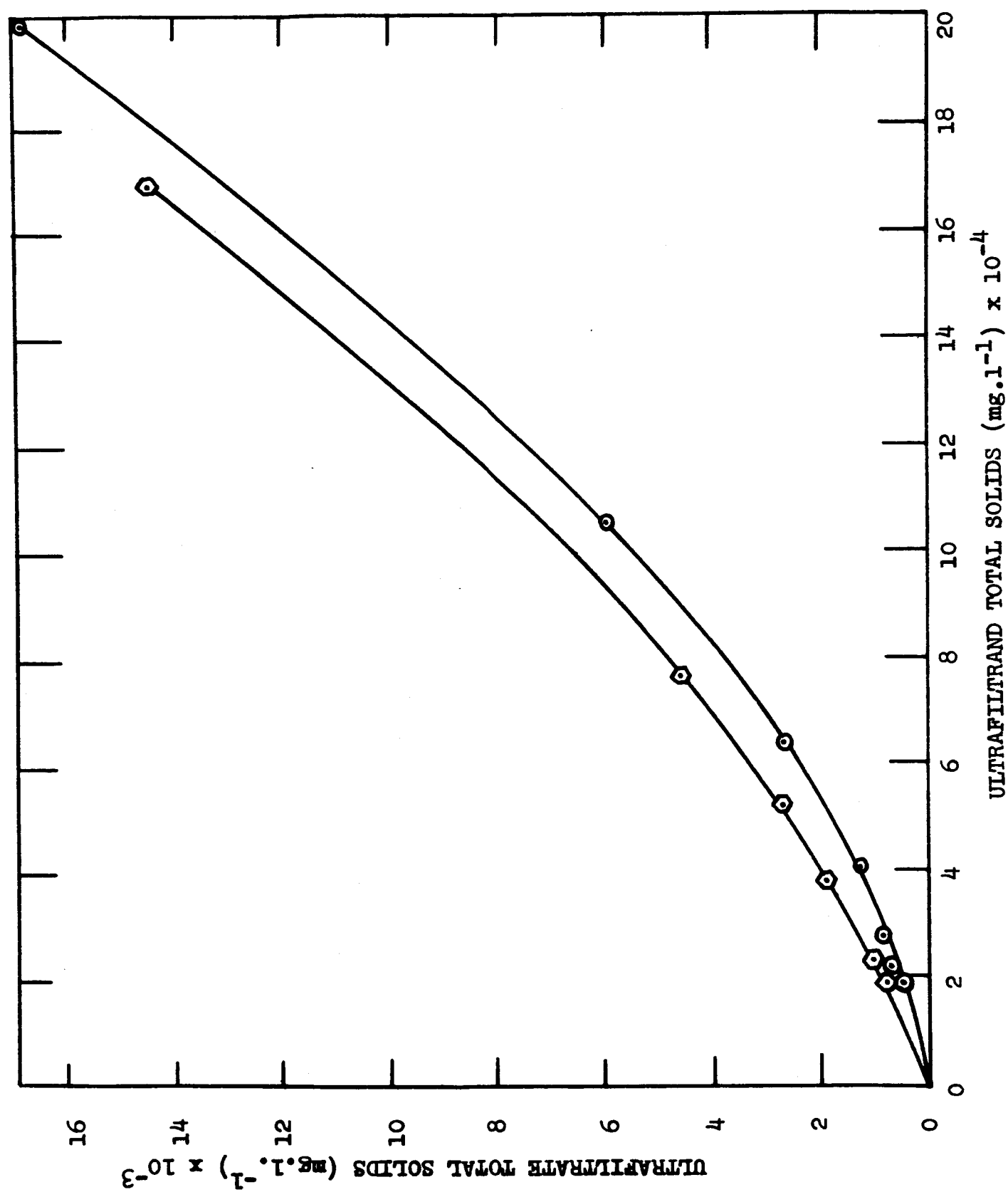


FIGURE XXIV Ultrafiltrate Total Solids as a Function of Ultrafiltrand Total Solids



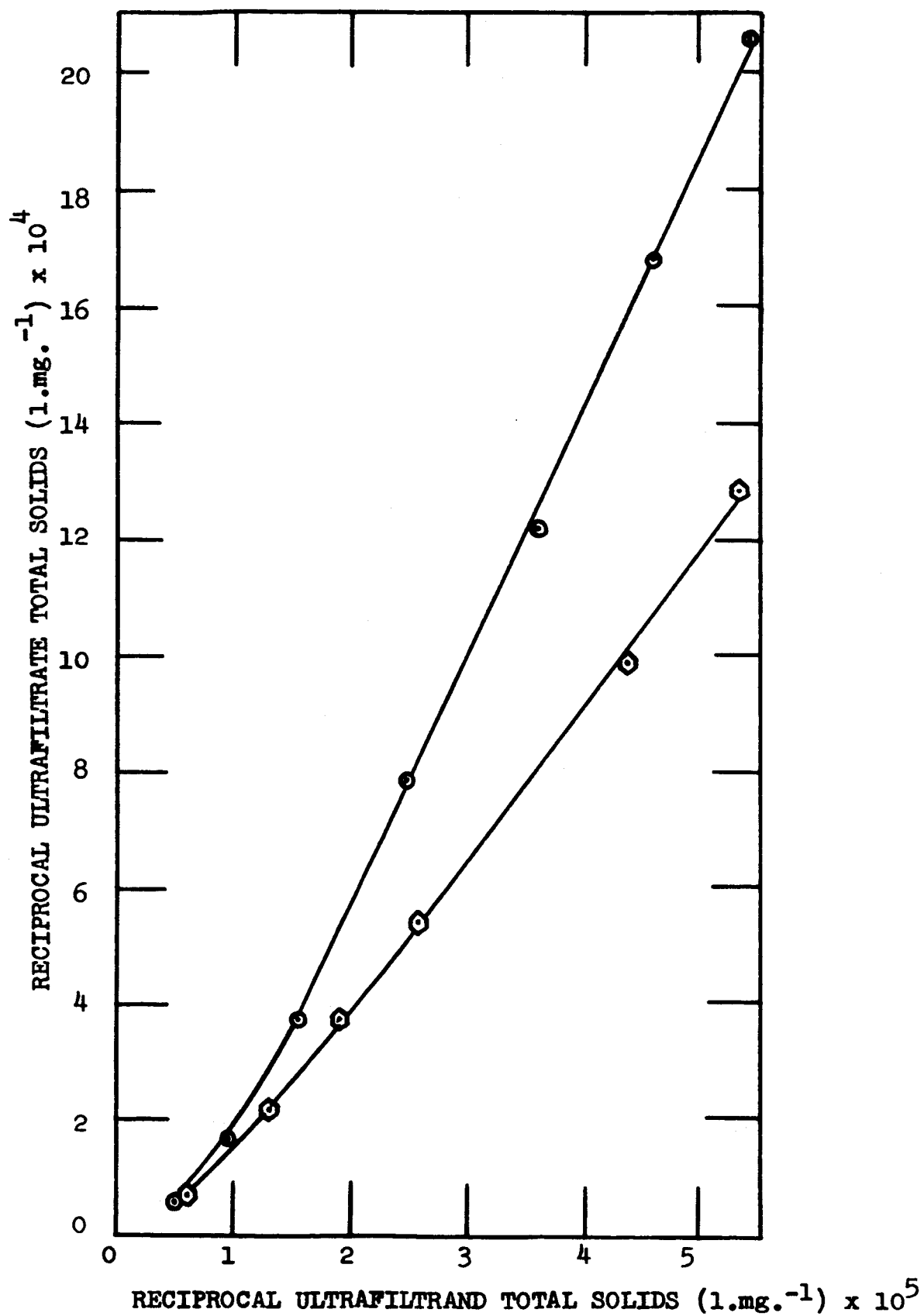


FIGURE XXV Ultrafiltrate Solid Contents as a Function of Ultrafiltrand Total Solids

ultrafiltrand concentration.

Figure XXIII constitutes a plot comparable to that prepared for the sodium chloride solution ultrafiltrand (see Figure XXI). The same linear nature of the graph is evident except in the more highly concentrated ultrafiltrand range.

Unfortunately, the membrane used in this series of experiments had been poorly cast and showed poor rejections, hence this series of data are of qualitative value only; the only analysis one can make is in terms of the reduction ratios, which are similar for both electrolyzed and artificial urine.

Experience acquired to date indicates the advisability of employing a design rationale in the prototype which is similar to that of the experimental apparatus. Appropriate modifications are necessary to fulfill weight minimization requirements.

Figure XXVI represents a systemic schematic diagram with preliminary weight estimates of all major components. Additional details relevant to these components include:

A. Electrolytic Cell:

Based on a feasible residence time of one hour and a sixteen-hour operating day, a cell volume of 300 cm.<sup>3</sup> would be required. Electrical power requirements are estimated at 2.28 watts per pound of urine. The total weight of the component should be less than five pounds.

B. Pump:

Preliminary information relative to a diaphragm pump possessing the requisite output characteristics has revealed the feasibility of securing a unit weighing approximately ten pounds and having a volume of 0.25 ft.<sup>3</sup> The operating pressure is specified as 150 atm. and the volumetric flow rate at four liters per hour.

C. Ultrafiltration Cell:

Basing calculations on a conservative estimate of the average flux as 1.65 lb.ft.<sup>-2</sup>hr.<sup>-1</sup>, a membrane area requirement is set at two ft.<sup>2</sup> It is further estimated that the component would have a volume of approximately 0.01 ft.<sup>3</sup> and weigh about three pounds.

Figure XXVII illustrates a possible ultrafiltration design scheme. The number of membrane wrappings and, therefore

**FIGURE XXVI Schematic Diagram of EUF System**

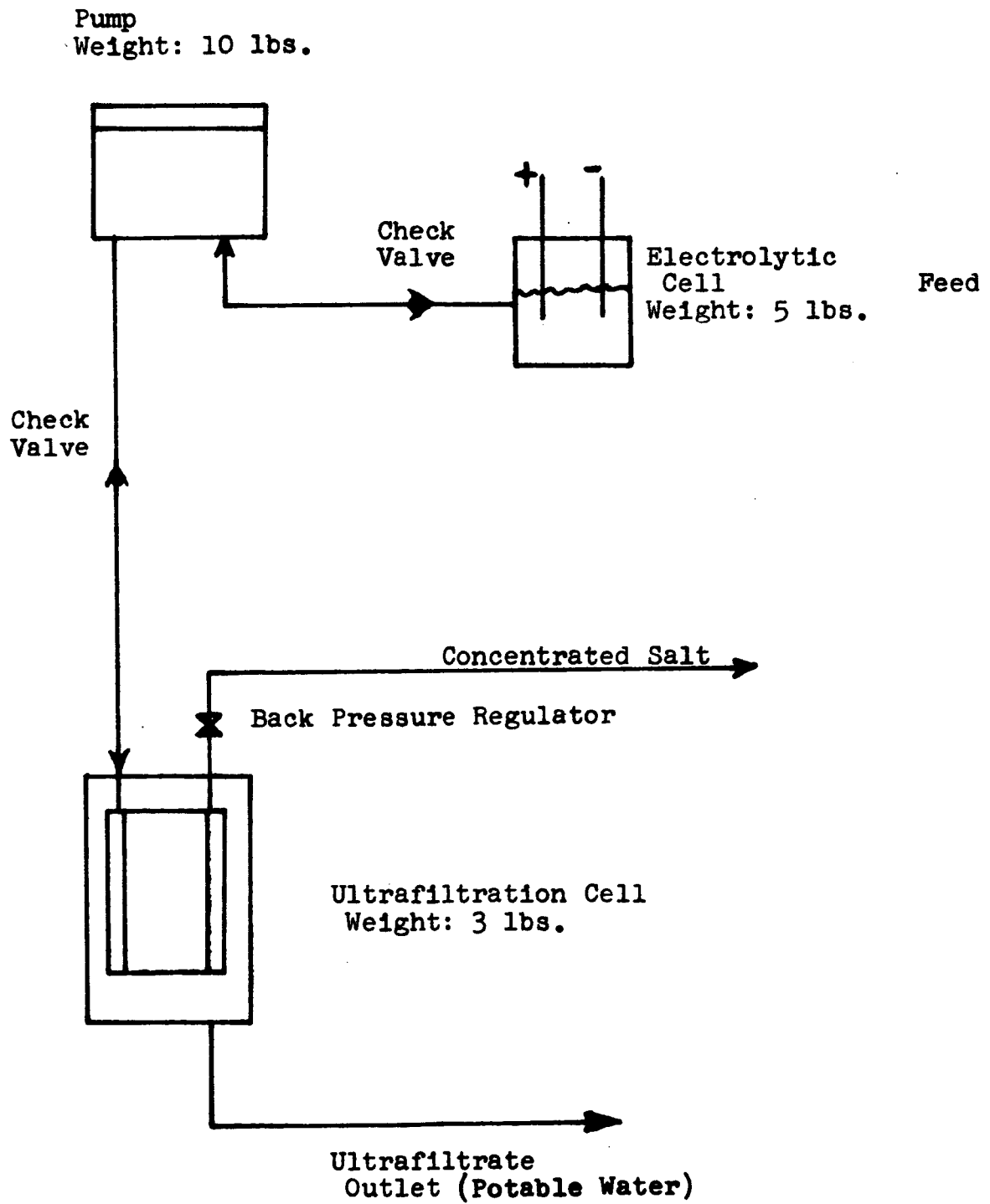
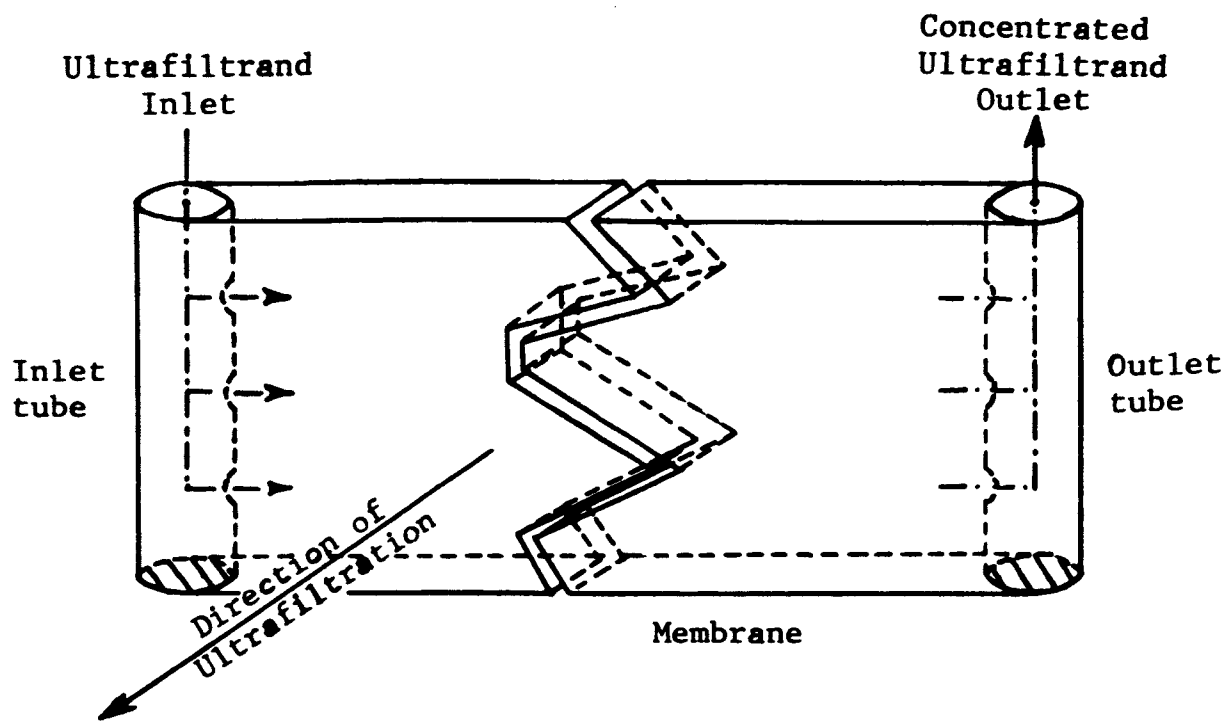
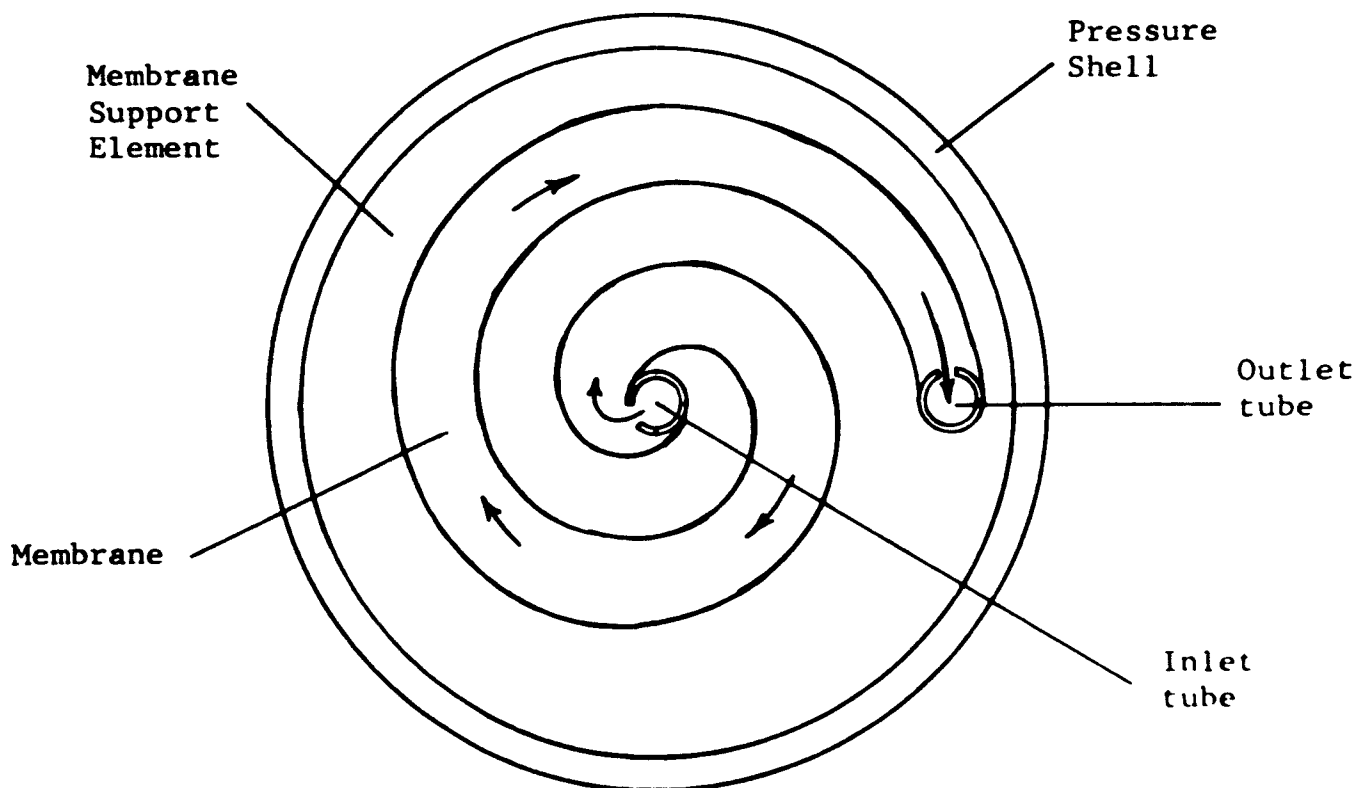


FIGURE XXVII Membrane Assembly



Uncoiled Membrane Assembly



Coiled Membrane Assembly

the available membrane area, to be fitted inside the pressure cell can be increased with little volume and weight penalty.

D. Valves and Tubings:

Two check valves, a back pressure valve and approximately one foot of tubing would be required. Their total weight contribution should be approximately one pound.

Regarding materials of construction, durable, light-weight, corrosion-resistant substances such as plastics, ceramics and titanium are programmed for use in the appropriate systemic components.

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